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CONTENT INDEX (vol 4)

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BEARING MATERIALS 1
BEER 12
BENZALDEHYDE 32
BENZENE 37
BENZOIC ACID 52
BENZYL ALCOHOL AND b-PHENETHYL ALCOHOL 59
BERYLLIUM AND BERYLLIUM ALLOYS 65
BERYLLIUM COMPOUNDS 75
BEVERAGE SPIRITS, DISTILLED 78
BIOPOLYMERS 93
- SURVEY 94
- ANALYTICAL TECHNIQUES 96
BIOSENSORS 106
BIOTECHNOLOGY 113
BIPHENYL AND TERPHENYLS 114
BISMUTH AND BISMUTH ALLOYS 122
BISMUTH COMPOUNDS 127
BLEACHING AGENTS 140
- SURVEY 141
- PULP AND PAPER 155
BLOOD, ARTIFICIAL 160
BLOOD, COAGULANTS AND ANTICOAGULANTS 170
BORON, ELEMENTAL 183
BORON COMPOUNDS 187
- BORON OXIDES, BORIC ACID, AND BORATES 188
- BORIC ACID ESTERS 213
- REFRACTORY BORON COMPOUNDS 218
- BORON HALIDES 222
- BORON HYDRIDES, HETEROBORANES, AND THEIR METALLA DERIVATIVES 227
- BORON HYDRIDES, HETEROBORANES, AND THEIR METALLA DERIVATIVES (COMMERCIAL ASPECTS) 259
- ORGANIC BORON-NITROGEN COMPOUNDS 261
BRAKE LININGS AND CLUTCH FACINGS 272
BROMINE 278
BROMINE COMPOUNDS 291
BTX PROCESSING 306
BUILDING MATERIALS 316
- SURVEY 317
- PLASTIC 326
BUTADIENE 340
BUTYL ALCOHOLS 355
BUTYLENES 361
BUTYRALDEHYDES 377
CADMIUM AND CADMIUM ALLOYS 384
CADMIUM COMPOUNDS 391
CALCIUM AND CALCIUM ALLOYS 399
CALCIUM COMPOUNDS 405
- SURVEY 406
- CALCIUM CARBONATE 410
- CALCIUM CHLORIDE 413
- CALCIUM SULFATE 418
CAPROLACTAM 426
CARBAMIC ACID 434
CARBIDES 437
- SURVEY 438
- CEMENTED CARBIDES 442
- INDUSTRIAL HARD CARBIDES 448
- CALCIUM CARBIDE 457
- SILICON CARBIDE 463
CARBOHYDRATES 473
CARBON 492
CARBON AND ARTIFICIAL GRAPHITE 494
- STRUCTURE, TERMINOLOGY, AND HISTORY 495
- BAKED AND GRAPHITIZED CARBON 497
- PROCESSING OF BAKED AND GRAPHITIZED CARBON 501
- PROPERTIES OF MANUFACTURED GRAPHITE 508
- APPLICATIONS OF BAKED AND GRAPHITIZED CARBON 513
- OTHER FORMS OF CARBON AND GRAPHITE 527
- ACTIVATED CARBON 529
- CARBON BLACK 539
- DIAMOND, NATURAL 557
- DIAMOND, SYNTHETIC 561
- NATURAL GRAPHITE 569

BEARING MATERIALS

For many centuries the application of materials for low friction and wear in sliding and rolling contacts primarily involved wood, stone, leather, iron, and copper. Almost all engineering materials have since been employed at one time or another in the continuing search for the best bearing material. Final selection is commonly a judgment based on the most essential material properties, ease of application, and cost.

Economic Aspects

Production trends for bearings and bearing materials closely parallel general industrial activity.

Ball and roller bearings represent the largest business segment with worldwide production estimated at $14 billion in 1988 (1). U.S. production, forecast for $3.6 billion in 1991, has fallen 5% annually for several years (2). This decrease is attributed largely to the slump in the automotive industry which represents 31% of the market for rolling-element bearings (3).

Despite this past downward trend, which has persisted in the United States since 1979 with modernization of large suppliers in Japan and Europe, growth of 2 to 2.5% is now expected into the mid-1990s. This reflects increased demand for some military applications and commercial aircraft, plus growing needs for farm and construction machinery (2). U.S. production of the relatively new ceramic ball bearings is expected to increase distinctively by about 50% yearly to reach $17 million in 1993 (3).

Other than for rolling-element bearings, only a few bearing types are of general commercial significance. U.S. shipments of plain bearings were $375 million in 1987 (4). Powdered metal bearing production is expected to be about $63 million in 1993, jewel bearings $13 million, and wood $14 million (3). Production of air bearings is expected to increase 20% annually and reach $76 million in 1993 for use in light-load, high speed applications such as air circulators in aircraft, lasers, and dental drills. Environmental questions have brought on diminished use of lead in recent years in lead babbitt, porous metal bearings, and related bearing materials.

Some other bearing materials find extensive use for which production volume is less well defined. Filled plastics such as nylon, acetal resin, PTFE, and phenolics are formed and molded into bearings in a wide variety of mechanical structures. Tin, lead, and bronze alloys are used for oil-film bearings in heavy industrial and power generating equipment, frequently in custom bearings manufactured directly as machine components.

Distinctive Property Requirements

Friction, Wear, and Compatibility. Even bearings operating primarily with full oil-film lubrication may rub the shaft during starting and stopping, at initial run-in, under high transient loads, and during interruption of lubricant supply. During this sliding contact, the bearing material must avoid either welding to the shaft or scoring and galling under the localized high surface strains and high temperature at microscopic asperities.

Comprehensive tests for compatibility of metallic elements rubbing against a common low carbon shaft steel gave the results of Figure 1. Cadmium and copper bridge two ratings in this comparison. Good scoring resistance was demonstrated only by those elemental metals which have atomic diameters at least 15% greater than iron to minimize atomic junctions and mutual solubility, and are in the B subgroup of the periodic table which implies covalent atomic bonds at any junctions rather than more tenacious metallic bonds (5). Although bearing alloys are much more complicated, their element content provides a guideline. Adding more of the good element, eg, lead in a copper alloy, generally improves score resistance; whereas more of the poor metal zinc will degrade score resistance (6).

Good	Fair	Poor	Very poor	
germanium	carbon	magnesium	beryllium	molybdenum
silver	copper	aluminum	silicon	rhodium
cadmium	selenium	copper	calcium	palladium
indium	cadmium	zinc	titanium	cerium
tin	tellurium	barium	chromium	tantalum
antimony		tungsten	iron	iridium
thalium			cobalt	platinum
lead			nickel	gold
bismuth			zirconium	thorium
			columbium	uranium

Fig. 1. Score resistance of elements against 1045 steel.

Various plastics and other nonmetallics also provide excellent compatibility, low friction, low wear, and good scoring resistance. Their application is usually limited to slow surface speeds, however, where their low thermal conductivity does not lead to overheating.

Antiweld and antiscoring characteristics can be described in fundamental terms for some simple systems. A preliminary rubbing test of a prospective bearing material provides a useful evaluation before actual use (7–9). Performance evaluation in the boundary–lubrication region, where the rubbing materials are only partially separated by a lubricant film, helps especially in establishing compatibility of the bearing material with both the mating material and the lubricant (7,8).

Ease of Embedding and Conformability. Hardness and modulus of elasticity of oil-film and boundary-lubricated bearing materials should be as low as possible while providing sufficient strength to carry the applied load. The resulting properties provide optimum compensation by the material for misalignment and other geometric errors. When a shift surface forces dirt, machining chips, or grinding debris against a bearing, the bearing material is required to absorb the foreign particles to minimize scoring and wear. Experimental observations rank materials in the same order as anticipated from Table 1 with low modulus of elasticity giving good embedability. The soft babbitts are unsurpassed for both embedability and conformability.

Table 1. Physical Properties of Sliding Bearing Materials

	Hardness[a]	Specific gravity	Tensile strength, MN/m^2[b]	Modulus of elasticity, GN/m^2[b]	Thermal conductivity, W/(m·K)	Coefficient of expansion, 10^{-6} °C
Metals						
lead babbitt	21	10.1	69	29	24	25
tin babbitt	25	7.4	79	52	55	23
copper lead	25	9.0	55	52	290	20
silver	25	10.5	160	76	410	20
cadmium	35	8.6		55	92	30
aluminum alloy	45	2.9	150	71	210	24

lead bronze	60	8.9	230	97	47	18
tin bronze	70	8.8	310	110	50	18
zinc alloy	95	5.1	320	79	125	
steel	150	7.8	520	210	50	12
cast iron	180	7.2	240	160	52	10
Porous metals						
bronze	40	6.4	120	11	29	16
iron	50	6.1	170		28	10
aluminum	H55[c]	2.3	100		137	23
Plastics						
nylon	M79[c]	1.14	79	2.8	0.24	80
acetal	M94	1.42	69	2.8	0.22	80
PTFE	D60[d]	2.17	21	0.6	0.24	130
phenolic	M100	1.36	69	6.9	0.28	40
polyester	D78[d]	1.45	59	2.3	0.19	95
polyimide	E52[c]	1.43	73	3.2	0.36	50
Other nonmetallics						
carbon graphite	75[e]	1.7	14	14	9	5
wood		0.68	8	12	0.19	5
rubber	65[f]	1.2	10	0.04	0.16	77
tungsten carbide	A91[c]	14.2	900	560	70	6
silicon nitride	1430[g]	3.2		310	17	3
Al_2O_3	2500[g]	3.9	210	340	24	8

[a] Brinell, unless otherwise noted.

[b] To convert MN/m^2 to psi, multiply by 145.

[c] Rockwell

[d] Shore Durometer.

[e] Shore Scleroscope.

[f] Shore A.

[g] Knoop.

Strength. An alloy too low in strength is prone to extrude under load, whereas too high strength may be accompanied by brittleness, poor embedding of foreign particles, and inability to conform to misalignment. In general, bearing surface hardness should be no greater than 1/3 to S the journal hardness to avoid self-propagating shaft scoring (10).

Fatigue strength is particularly important with reciprocating loads such as those encountered in connecting rods and main bearings for internal combustion engines. This requirement often leads to use of aluminum, copper–lead, or bronze bearing material for automotive and diesel engines. A thin babbitt overlay is commonly applied for improved compatibility. Table 2 gives an approximate guide for various materials (6).

Table 2. Fatigue Strength of Typical Bearing Metals

Material	Dynamic load capacity[a], MPa[b]
bronze	100
silver	80
copper	80
copper lead with tin	70
aluminum alloys	25–60
copper lead	20–50
thin babbitt	10–25
thick babbitt	5–10

[a] Approximate maximum.

[b] To convert MPa to psi, multiply by 145.

High fatigue strength is especially critical in ball and roller bearings. The cycling, high contact stress imposed by the rolling elements demands materials with high hardness and the best available fatigue strength.

Material strength is but one factor in determining maximum load that can be carried by a bearing material. Load capacity is equally related to design details, lubrication, and general application experience.

Corrosion Resistance. Materials containing lead, cadmium, copper, and zinc are susceptible to corrosion by the organic acids and peroxides formed in lubricating oil during its oxidation in service. This difficulty can be minimized by selecting oils with good oxidation inhibitors, by keeping the operating temperature low, and with periodic oil changes.

Individual bearing materials must be considered for operation in water, corrosive chemical fluids, high temperature gases, and liquid metals.

Thermal Properties. Conducting frictional heat out through a bearing can be a significant requirement, particularly for high speeds. Poor heat transfer commonly restricts use of plastic bearings at high speeds where charring of the plastic and overheating of the journal can be expected.

For operation over a range of temperatures, matching thermal expansion coefficients of the bearing and shaft is important to maintain suitable clearance. As an example for accommodating unlike coefficients, shrinking carbon–graphite with its low expansion coefficient into a steel shell helps minimize loss of clearance with a steel shaft at elevated temperature. Bronze and aluminum applications should also take into account differences between their thermal expansion and that of steel. General drop in bearing material strength should also be taken into account for elevated temperatures.

Oil-Film Bearing Materials

Lubricant-film bearings primarily employ the white-metal babbitts, and a variety of copper and aluminum alloys. Since steel and cast iron structural parts are frequently used as oil-film bearing materials, they are also briefly covered along with silver, zinc, and cadmium which find limited use. For small bearings and bushings in light-duty and intermittent service, materials with self-lubricating properties are commonly used.

Babbitt Metals. High lead and tin alloys patented by Isaac Babbitt in 1839 offer a superior combination of compatibility, conformability, and

embedability when used as a bearing material lining in a steel or bronze shell. Typical babbitt compositions covered by ASTM B23 and SAE specifications (11,12) are given in Table 3 and physical properties are provided in Table 4.

Table 3. Composition of Babbitts

Metal, %	Tin base			Lead base		
	SAE 11	SAE 12,[a] ASTM B23-2	ASTM B23-3	SAE 13[b]	SAE 14, ASTM B23-7	SAE 15,[c] ASTM B23-15
Cn	86[d]	88.25[d]	84	5–7	9.25–10.75	0.9–1.25
Sb	6–7.5	7–8	8	9.05–11	14–16	14–15.5
Cu	5–6.5	3–4	8	0.5[e]	0.5[e]	0.5[e]
Fe[e]	0.08	0.08	0.08			
As[e]	0.1	0.1	0.1	0.25	0.6	0.8–1.2
Bi[e]	0.08	0.08	0.08			
Zn[e]	0.005	0.005	0.005	0.005	0.005	0.005
Al[e]	0.005	0.005	0.005	0.005	0.005	0.005
Cd[e]				0.05	0.05	0.05
Pb	0.5[e]	0.5[e]	0.35[e]	balance	balance	balance
others[e]	0.2	0.2		0.2	0.2	0.2

[a] Tin alloy *[12672-06-9]*.
[b] Lead alloy *[63936-49-2]*.
[c] Lead alloy *[8052-78-6]*.
[d] Minimum amount.
[e] Maximum amount.

Table 4. Properties of Cast Babbitts

Property	Tin base		Lead base
	ASTM Grade 2	ASTM Grade 3	ASTM Grade 15
specific gravity	7.39	7.46	10.05
melting point, °C	241	240	248
temp of complete liquefaction, °C	354	422	281
Brinell hardness number			
20°C	24.5	27.0	21.0
100°C	12.0	14.5	13.0
150°C	8.7	10.8	
tensile strength, MN/m^2[a]			
20°C	103	121	
100°C	60	68	44
150°C			26
fatigue strength, MN/m^2[a]			
20°C	29	32	24
100°C		17	
150°C	14	8.2	

[a] To convert MN/m^2 to psi, multiply by 145.

Tin babbitts are based on the tin–antimony–copper system and commonly contain about 3–8% copper and 5–8% antimony. Within a soft, solid-solution matrix of antimony in tin are dispersed small hard particles of the intermetallic copper–tin, Cu_6Sn_5 *[12019-69-1]* (13).

Greater amounts of copper increase the proportion of needles or stars of Cu_6Sn_5 in the microstructure. Increase in antimony above 7.5% results in antimony–tin cubes. Hardness and tensile strength increase with copper and antimony content; ductility decreases. Low percentages of antimony (3–7%) and copper (2–4%) provide maximum resistance to fatigue cracking in service. Since these low alloy compositions are relatively soft and weak, compromise between fatigue resistance and compressive strength is often necessary.

Despite their higher cost, tin babbitts are often preferred over lead for their excellent corrosion resistance, easy bonding, and less tendency for segregation. SAE 12 (ASTM Grade 2) is widely used in both automotive and industrial bearings (13); ASTM Grade 3 and SAE 11 also find extensive industrial use.

Lead babbitts, based on the lead–antimony–tin system, contain 9–16% antimony and up to 12% tin. Their structure consists of hard, cuboid crystals of SbSn in a eutectic matrix of the three metals (13). To minimize segregation in casting, 0.5% copper is usually added. SAE 15 also contains 1% arsenic for a finer grain structure. SAE grades 13 through 16 contain sufficient tin and antimony to provide reasonable corrosion resistance. Corrosion problems can usually be avoided by using oxidation-inhibited lubricating oils and regular relubrication to avoid buildup of acidic oil oxidation products.

Arsenical SAE 15 babbitt has been used in many automotive bearings for its low cost, resistance to fatigue, and better high temperature properties. This composition also gives excellent service in large hydroelectric generator thrust bearings. With a higher tin content of 10% for improved corrosion resistance, SAE 14 is frequently used in railroad, industrial, and automotive applications. SAE 13 is used as a softer babbitt.

Babbitt application methods vary greatly. Most high performance bearings in automotive engines use plated lead babbitt of 10% tin and about 3% copper as covered by SAE 19 and SAE 190 specifications (6).

For larger bearings in electric motors, turbines, compressors, and other industrial equipment, centrifugally cast babbitt is commonly finished to 1.5–10 mm thickness. For a sound babbitt bond, careful attention is required at each step: cleaning the bearing shell, rinsing, fluxing, tinning, babbitt casting, and finally quenching. With smaller bearings and bushings, such as used in automotive engines and small electric motors, a bimetal strip is first produced by casting the babbitt on a continuous steel strip. After forming oil-distributing grooves and broaching oil feed holes, the strip is cut to size and the individual segments are rolled into finished bearings.

For high fatigue strength in automotive bearings, a very thin layer of babbitt is desirable so that much of the load is taken on a stronger backing material. Relative improvement in fatigue resistance was found to be as follows with tin babbitt (14):

Babbitt thickness, mm	Relative fatigue resistance
1.00	1
0.50	1
0.25	1.5
0.13	3.2
0.08	4.6

For heavy-duty reciprocating engines, three-layer strip bearings are frequently used. These consist of a low carbon steel backing; an intermediate layer (about 0.3–0.8 mm thick) of copper–nickel, copper–lead, leaded bronze, aluminum, or electroplated silver; and a thin 15–25 micrometer overlay of SAE 19 or SAE 190 lead babbitt added by electroplating or precision casting. The thin babbitt is sometimes considered to help only run-in, after which the load is carried by the higher strength intermediate layer.

Copper Alloys. Most copper-base bearing materials can be grouped in four classes: copper–lead, leaded bronze, tin bronze, and aluminum and other high strength bronzes (15,16). Characteristics of typical materials are given in Table 5. Alloys at the top of the list have higher lead content and better compatibility. Strength, hardness, and wear resistance increase as tin, aluminum, and iron are added in going down the table.

Table 5. Properties of Bronze and Copper-Bearing Alloys[a]

Material	SAE alloy number[b]	CAS Registry Number	Nominal composition, % Cu	Sn	Pb	Zn	Hardness (Brinell)	Tensile strength, MN/m^2[c]	Yield strength, MN/m^2[c]	Max operating temp, °C	Max load, MN/m^2[c]
copper–lead	480		65		35		25	55		180	14
copper–lead	48		70		30		28	59		180	14
high leaded tin bronze	CA943	*[54425-87-5]*	70	5	25		48	170	83	210	22
semiplastic bronze	CA938A	*[12774-00-4]*	78	6	16		52	190	97	230	22
	} CA938B						62	240	160	230	22
leaded red brass	CA836	*[12773-58-9]*	85	5	5	5	60	240	100	230	24
bearing bronze	CA932A	*[39372-59-3]*	83	7	7	3	58	230	110	240	28
	CA932B	*[65188-00-3]*					72	300	190	240	28
phosphor bronze	CA937A	*[12767-50-9]*	80	10	10		60	240	120	240	28
	CA937B	*[12773-99-8]*					80	280	180	240	28
gunmetal	CA905A	*[12605-83-3]*	88	10		2	65	280	120	250+	28
	CA905B						92	360	200	250+	28
Navy G	CA903	*[12682-57-4]*	88	8		4	68	280	120	250	29
leaded gun metal	CA927A	*[39281-90-8]*	88	10	2		65	280	120	250	29
	} CA927B						86	340	170	250	29
aluminum bronze	CA954	*[11114-34-4]*	85	(4 Fe, 11 Al)			195	620	280	250+	31

[a] Ref. 17.

[b] Suffix A denotes sand cast, B denotes continuous cast.

[c] To convert MN/m^2 to psi, multiply by 145.

Although copper alloys are excellent as bearing materials for many applications, their utility is limited at high surface speeds and with marginal lubrication by the tendency for formation of a copper transfer film on a mating steel shaft. At surface speeds above about 8–15 m/s (1500–3000 ft/min), selective plucking may occur with softer copper material from hotter load zones of the bearing surface welding in lumps onto the cooler, stronger copper transfer film on a steel journal. Care as to adequate lubricant feed, lubricant selection, increased journal hardness, and a thin overlay of a "good" compatibility metal from Figure 1 will help avoid this problem.

With binary copper–lead, the continuous copper phase provides the primary load support while pockets of 20–50% lead supply a continuous lead surface film. Tin content of 3–5% is commonly incorporated with the lead to minimize corrosion. Copper–lead alloys, either cast or sintered on a steel back, provide good fatigue resistance for heavy-duty main and connecting rod bearings for auto, truck, diesel, and aircraft engines.

Leaded bronzes are used in large volumes for a wide range of applications as cast bushings, or cast or sintered on a steel backing. Containing about 5–25% lead, leaded bronzes commonly incorporate up to 10% tin for higher strength, higher hardness, and better fatigue resistance than copper–leads. The 10% tin–10% lead phosphor bronze has been a traditional selection for applications in steel mills, household appliances, pumps, automotive piston-pin bearings, and trunions. This 10–10 bronze is being replaced in many applications with CA932 (SAE 660) containing 3% zinc for easier casting. SAE 660 is available in continuously cast rods and tubing for easy forming into final bearing shapes. Lower cost of CA836 brings it into use at low to moderate loads and speeds.

Higher hardness tin bronzes, such as the gun metal alloys in Table 5, require reliable lubrication, good alignment, and 300 to 400 minimum Brinell shaft hardness. Cast tin bronze bushings are used in high load, low speed service in trunion bearings, gear bushings in farm machinery, earth-moving equipment, rolling mills, and in automobile engines for connecting rod bearings, valve guides, and static bearings. With their inherent strength, they need not be cast on a steel backing.

Aluminum bronzes with their excellent strength provide shock and wear resistance in bushings and bearing plates for machine tools, aircraft landing gear, and other rather special applications. Age-hardened beryllium copper containing about 2% beryllium also provides high strength and has been used in airframe applications for bearing stresses as high as 315 MN/m^2 (~50,000 psi) (15). With their poor score resistance and lack of embedability, higher shaft hardness is required together with good alignment and adequate lubrication.

Aluminum. Aluminum bearing alloys such as listed in Table 6 are characterized by high fatigue strength, excellent corrosion resistance, high thermal conductivity, and low cost. Although they find only minor use in general industrial applications because of their limited compatibility, aluminum bearings are widely employed in automotive and diesel engines, reciprocating compressors, and aircraft equipment (18). Adequate lubrication, good journal finish, and a hardened shaft of Rockwell hardness R_B 85 or higher are required.

Table 6. Aluminum Bearing Alloys

Alloy	Nominal composition, %[a] Sn	Cu	Ni	Si	Cd	Type of bearing
SAE 770, cast	6.5	1	1			solid
SAE 780, rolled	6.5	1	0.5	1.5		bi- or trimetal
SAE 781, wrought				4	1	bi- or trimetal
reticular Sn–Al	20	1				bimetal
silicon–aluminum		1		11		trimetal

[a] Remainder in each case is aluminum.

SAE 780 tin, silicon, and copper alloy, and SAE 770 using tin, copper, and nickel are aluminum alloys which have been widely used in medium- and heavy-duty diesels (6). With silicon and cadmium incorporated for improved compatibility, both SAE 781 and 782 are used as an 0.5 mm to 3.0 mm overlay on a steel backing with a thin electroplated babbitt overlay. Traditional 6% tin–aluminum is also used as the SAE 780 alloy with an overlay. Eleven percent silicon alloys are used for highly loaded diesel bearings in Europe.

Special aluminum alloys have been developed with much higher tin or lead content to eliminate the need for an overlay. Reticular tin–aluminum containing 1% copper has exhibited success in automotive and diesel engine bearings in Europe (19). As this high tin composition solidifies, tin precipitates at grain boundaries to give an initially weak alloy. Cold working followed by heat treatment then causes the tin to withdraw into discrete pockets within an aluminum matrix.

Aluminum babbitt has been a U.S. alternative (6,20). On cooling this molten material, 8% lead separates from the aluminum as globules at the surface for improved antiscoring properties. More recently, a sintered lead–aluminum containing 8.5% lead, 4% silicon, 1.5% tin, and 0.5% copper has been developed for automotive use.

Cast Iron and Steel. Bearing surfaces can be machined directly in gray cast iron structural parts for light loads and low speeds. The flake graphite in the cast iron develops a surface glaze for carrying loads up to about 1.0 MPa (145 psi) at surface speeds up to about 0.8 m/s in pivots, lightly loaded transmissions, camshafts, and machinery bearings. With good alignment, clean and copious oil feed, and hardened and ground journals, loads range up to 4.5 MPa (650 psi) for main bearings in cast iron refrigeration compressors, and up to 5.5 MPa (800 psi) for connecting rods (21). A phosphate etched surface is often applied as an aid for initial run-in. Guide surfaces and journal bearings can also be inexpensively machined in structural steel parts for loads up to 1.4 MPa (200 psi) at speeds up to 0.8 m/s.

Other Metals. Materials employed for hydrodynamic oil film bearings are primarily those covered above, but silver, zinc, and cadmium find some use.

Silver bearings have given excellent results in high performance reciprocating aircraft engines, and their specialized use continues in diesels and superchargers (6). These bearings normally consist of about 0.3 mm of silver electrodeposited on a steel backing with an 0.025 to 0.100 mm overlay of lead–indium for improved embedability and antiscoring properties. High cost of silver has generally led to substitution of other intermediate high fatigue strength layers such as aluminum, copper–lead, or bronze. Unique self-healing and excellent compatibility in rubbing with steel make thin silver electroplated coatings useful as bearing materials under severe sliding conditions in a variety of special or experimental machines.

Zinc alloys are finding renewed interest for lower cost and better wear life as replacements for SAE 660 and other bronzes (17). About 10–30% aluminum is introduced for improved properties in both oscillating and many rotating applications at speeds up to 7 m/s (1400 ft/min) at temperatures up to 90–125°C.

Cadmium alloys had been used in some passenger car and truck engines, and in some roll neck bearings for steel mills. Despite high temperature fatigue strength somewhat superior to babbitt and excellent compatibility with steel, poor corrosion resistance to oxidized oil and high cost have gradually led to phasing out of cadmium bearings.

Dry and Semilubricated Bearing Materials

Porous bronze and iron, a variety of plastics, carbon–graphite, wood, and rubber are widely used in dry sliding or under conditions of sparse lubrication. These materials have commonly allowed design simplifications, freedom from regular maintenance, reduced sensitivity to contamination, and good performance at low speeds and with intermittent lubrication. Although these materials are often used dry or with sparse lubrication, performance normally improves the closer the approach to full-film lubrication.

Porous Metals. Porous bearings consisting of pressed and sintered bronze, iron, or aluminum alloy powder are produced at a rate of millions per day for a wide variety of uses in small electric motors, household appliances, business machines, machine tools, automotive accessory units, and farm and construction equipment (17,22,23). Sleeve bearings, flanged bushings, thrust washers, and spherical self-aligning bearings are commercially available in hundreds of variations for shaft sizes ranging from 1.6 to 150 mm diameter.

Traditional powder metal bearings (Table 7) consist of bronze of 90% copper–10% tin. The common pore volume of 20–30% is usually impregnated with an oxidation-resistant oil of SAE 30 viscosity (22). High porosity with high oil content is favored for higher speed, light load applications. Lower porosity with up to 3.5% added graphite is desirable for low speeds and oscillation where oil-film formation is difficult.

Table 7. Operating Limits for Porous Metal Bearings

Porous metal	Nominal composition, wt %	Load limit, P, MN/m^2[a] Static	Dynamic	Speed limit, v, m/s	Pv limit MN/(m·s)
bronze	Cu 90, Sn 10	59	28	6.1	1.8[b]
iron		52	25	2.0	1.3
iron–copper	Fe 90, Cu 10	140	28	1.1	1.4
iron–copper–carbon	Fe 96, Cu 3, C 0.7	340	56	0.2	2.6
bronze–iron	Fe 60, Cu 36, Sn 4	72	17	4.1	1.2
aluminum		28	14	6.1	1.8

[a] To convert MN/m^2 to psi, multiply by 145.

[b] Approximately equivalent to 50,000 psi × ft/min limit often quoted by U.S. suppliers.

Porous iron is extensively used for its lower cost and higher load capacity at low speed. Small additions of carbon and up to 20% copper provide higher strength and improved compatibility. Up to 40% of 90–10 bronze powder incorporated with iron powder also reduces the cost compared to conventional porous bronze. Porous aluminum containing 3–5% copper, tin, and lead finds limited use. In some applications porous aluminum provides cooler operation, better conformability, lower weight, and longer oil life than porous bronze or iron. Impregnation of sintered iron bearings with perfluoropolyether oil gives much longer life than conventional petroleum oil at 150°C (24).

Limiting conditions for operating porous metal bearings are given in Table 7. Maximum unit load at low speed and maximum surface speed at light

load are listed in the first two columns. For intermediate operating conditions, load and speed limits are combined in a limiting *Pv* factor. With a given coefficient of friction, this *Pv* product of unit load *P* (MPa, psi) and surface velocity *v* (m/s, ft/min) gives a measure of surface frictional heating and temperature rise.

As a generality, porous metal sleeve bearings tolerate *Pv* levels up to 1.8 MN/(m·s) (50,000 psi·ft/min). *Pv* levels for thrust bearings should not exceed about 20% of the sleeve bearing limit. Variations of oil viscosity, oil content, graphite content, and other material and property details also influence the approximate operating limits given in Table 7.

Plastics. Almost all commercial plastics find some use both dry and lubricated for sliding at low speeds and light loads; the most commonly used thermoplastics are nylon, acetal resins, and polytetrafluoroethylene (PTFE). Typical thermosetting resins for bearing applications are phenolics, polyesters, and polyimides. Table 8 compares the characteristics of plastic bearing materials with those of graphite, wood, and rubber which find use in somewhat similar applications.

Table 8. Representative Limiting Conditions for Nonmetallic Bearing Materials

Material	CAS Registry Number	Max temperature, °C	*Pv* limit, MN/(m·s)[a]	Max load, *P*, MN/m²[b]	Max speed, *v*, m/s
Thermoplastics					
nylon	*[32131-17-2]*	90	0.90	5	3
filled		150	0.46	10	
acetal	*[37273-87-3]*	100	0.10	5	3
filled			0.28		
PTFE	*[9002-84-0]*	250	0.04	3.4	0.3
filled		250	0.53	17	5
fabric			0.88	400	0.8
polycarbonate	*[24936-68-3]*	105	0.03	7	5
polyurethane	*[27416-86-0]*	120			
polysulfone	*[25135-51-7]*	160			
Thermosetting					
phenolics	*[9003-35-4]*	120	0.18	41	13
filled		160	0.53		
polyimides		260	4		8
filled		260	5		8
Others					
carbon–graphite		400	0.53	4.1	13
wood		70	0.42	14	10
rubber		65		0.3	20

[a] See Table 7.

[b] To convert MN/m² to psi, multiply by 145.

As with porous metals, service limits for nonmetallic bearings commonly include a *Pv* load-speed limit as a measure of maximum tolerable surface temperature. Since wear volume in dry sliding is approximately proportional to total load and distance traveled, *Pv* also becomes a measure of radial wear depth *W* in the sleeve bearing relation $W = K(Pv)t$ where *t* is the operating time. Typical values of wear factor *K* are given in Table 9. Added fillers can raise the *Pv* limit for many unfilled plastics by a factor of 10–1000 and more (25). Common fillers include inorganic powders such as clay, glass fibers, graphite, molybdenum disulfide, powdered metal, and also silicone fluid as an internally available lubricant (26).

Table 9. Wear Factors for Plastic Bearings[a]

Material	Wear factor *K*, fm²/N	
	No filler	Filled[b]
nylon-6,6	4.0	0.24
PTFE	400	0.14[c]
acetal resin	1.3	4.9
polycarbonate	50	3.6
polyester	4.2	1.8
poly(phenylene oxide)	60	4.6
poly(phenylene sulfide)	10.9	4.8
polysulfone	30	3.2
polyurethane	6.8	3.6

[a] Ref. 25.

[b] With 30 wt % glass fiber, unless otherwise noted.

[c] 15% glass fiber.

As an example in estimating wear rate in a nylon bushing consider a 10-mm diameter shaft running 900 rpm (0.47 m/s) under 0.5×10^6 N/m² (70 psi) load. The *Pv* of 0.235×10^6 N/m²·m/s(6510 psi·fpm) and $K = 0.24 \times 10^{-15}$ m²/N for filled nylon in Table 9 gives a wear rate of 0.20 mm/1000 h. Since *Pv* test results vary widely, these wear estimates are only guides. For maximum utility, the test materials, finishes, temperature, load, speed, and lubrication should duplicate as nearly as possible those in the planned application.

Injection-molded nylon and acetal resin provide the least expensive small bearings for thousands of lightly loaded applications in household appliances, office machines, toys, textile and food machinery, and instruments. Nylon requires little or no lubrication, provides low friction, and gives quiet operation (see POLYAMIDES, PLASTICS). Cold flow at high loads is minimized either by applying the nylon as a thin layer in a steel backing, or by incorporating in the nylon fillers such as graphite, glass fibers, or inorganic powders. Acetal resins (qv) are used in many applications similar to those for nylon in automotive, appliance, and industrial bearings. Polyacetal and ultrahigh molecular weight polyethylene (UHMWPE) are often used to mold inexpensive housings, gears, and other machine elements of which the bearings are a portion.

Polytetrafluoroethylene (PTFE) often provides the lowest coefficient of friction available with plastics, commonly 0.05–0.10 at low speeds, and has a wide service temperature range from cryogenic levels to about 200–250°C. Solid PTFE is, unfortunately, relatively poor in accepting supplementary lubrication. Conventional petroleum oils do not wet PTFE well, and any oil present tends to increase wear rate by interfering with back-and-forth interchange of wear fragments between the PTFE and its normal transfer layer on a sliding steel surface (see FLUORINE COMPOUNDS, ORGANIC,

POLYTETRAFLUOROETHYLENE).

For low speeds and semistatic use, PTFE is often applied as a woven fabric for improved resistance to cold flow and for much higher load capacity in automotive ball and socket joints, aircraft controls, bridge bearings, and electrical switchgear. For this purpose, a secondary fiber such as polyester, glass, or cotton is interwoven with PTFE to enable a strong supporting bond to steel backing. Conventional oils and greases often improve performance of PTFE composites.

Inexpensive phenolic resins (qv) are commonly used as composites with cotton fibers, cellulose, glass fibers, graphite, PTFE, and metal oxides. Higher processing cost of phenolics and polyesters generally restricts their use to larger bearings; below 50-mm bore size injection-molded thermoplastics are more common for their lower cost. Phenolic bearings have replaced metal and wood in such diverse applications as bearings for rolling mills, ship propeller shafts, electrical switchgear, and construction equipment. Their low thermal conductivity requires an adequate supply of oil or water to avoid overheating at high speeds and high loads; clearances must be generous to allow for some swelling by the fluids. In small applications such as instruments, appliances, and business machines, bearings are often simply formed as holes in phenolic or other plastic structural elements.

A number of other plastics are available for special uses at high temperatures. Most familiar are polyimides (qv), polysulfones, and poly(phenylene sulfide) (PPS) (see POLYMERS CONTAINING SULFUR). Despite their promise, widespread use has been limited by processing difficulty, high cost, and relatively poor room temperature properties. Polyimide molding compounds employing graphite and other fillers have found use in ball bearing retainers, bearing seals, aircraft bushings, and piston rings at temperatures up to 260°C.

Wood. Although lignum vitae and oil-impregnated maple and oak are useful up to 70°C, they have largely been replaced as bearing materials by porous metals, plastics, and rubber. Typical application of wood bearings are with water and other low viscosity fluids at relatively low speeds in pumps, conveyors, hydraulic turbines, food and chemical processing, and ship propeller shafts (27).

Carbon–Graphite. Carbon–graphites having a wide range of properties are manufactured by high pressure molding followed by curing at up to 1440°C of mixtures of graphite powder, petroleum coke, lamp black, and coal tar pitch. The resulting 5–20% porosity is selectively impregnated with phenolic or epoxy resins (qv), copper, babbitt, bronze, glass, or silver to give a wide range of strength, hardness, and wear resistance (28) (see CARBON, CARBON AND ARTIFICAL GRAPHITE).

Common uses include: pump bearings for water, gasoline, and solvents having low viscosity; high temperatures up to 400°C in conveyors and furnaces; and in food, drugs, and other machinery where oil and grease contamination must be avoided.

A hard, rust-resistant shaft of at least 0.25 micrometer finish is usually required. Common shaft surfaces are hardened tool steel, chrome plate, high strength bronze, and carbide and ceramic overlays. Test results over a broad speed range from 0.05 to 47 m/s (10 to 9200 fpm) indicate that a coefficient of friction of 0.16–0.20 and a wear factor of 14×10^{-16} $m^2/N(70 \times 10^{-10}$ $in.^3 min/ft\text{-}lb\text{-}h)$ are typical for dry operation of well applied grades of carbon–graphite (29).

Rubber. Synthetic rubber is commonly used in a fluted construction with a series of axial rubber segments separated by longitudinal water grooves, all enclosed in a rigid bronze cylindrical shell. The high degree of resilience of the rubber and its resistance to wear by abrasives bring these bearings into use for marine propeller shafts, water pumps and turbines, and conveyors for slurries of gravel, sand, and ores.

Noncorrodible shaft surfaces or shaft sleeves of bronze, stainless steel, Monel, or chrome plate are commonly employed with a rubber bearing.

High Temperature Materials

As the temperature limits for lubricating oils (150–250°C) and solid lubricants (350–400°C) and solid lubricants (350–400°C) are exceeded, bearing materials must accommodate either dry, low speed sliding or operate with very poor lubricants such as gas, pressurized water, or liquid metals. This involves new frontiers as continually higher temperatures are being encountered by bearings in gas turbines, diesel engines, automotive engines, supercharges, nuclear plant equipment, and rocket engines. Prototype testing is commonly required as a final step in bearing material selection.

High temperature strength often leads to selection of alloys such as those in Table 10 for use from 500–850°C (30). Although wear of these materials is often high at ordinary temperatures, a transition temperature is encountered above which wear drops (31). Above this transition temperature, a smooth surface oxide forms with sufficient rapidity to eliminate significant metal-to-metal contact. Following are approximate transition temperatures for a number of metals:

steel	185°C
molybdenum	460°C
titanium	575°C
chromium	630°C
nickel	630°C

Table 10. Hard Metals and Superalloys for High Temperature Bearings[a]

Material	CAS Registry Number	Up to, °C
Mo alloys, TZM		500
tool steels		500
nitrided steels		500
Hastelloy C[b]	*[12605-85-5]*	750
Stellite 6	*[11105-35-4]*	750
Stellite Star J[c]	*[53800-30-9]*	750
Inconel X	*[11145-80-5]*	850
Stellite 19	*[11105-37-6]*	850
Rene 41[d]	*[11068-84-1]*	850
Tribaloy T-400[e]	*[51141-95-8]*	850

[a] Ref. 30.

[b] 57% Ni, 17% Mo, 16% Cr, 5% Fe + Mn.

[c] 43% Co, 32% Cr, 17% W, 3% Fe + Ni, C, Mn, Si.

[d] 55% Ni, 19% Cr, 10% Co, 10% Mo, 3% Ti + Al, Fe, Si, Mn, C, B.

[e] 62% Co, 28% Mo, 8% Cr, 2% Si.

Table 11 gives order of magnitude wear rates for high temperature materials sliding against themselves in pin-on-disk tests (30).

Table 11. Order of Magnitude of the Specific Wear Rates for Various High Temperature Materials Sliding Against Themselves at 500°C[a]

Material	Specific wear rate ($mm^3/N{\cdot}m$)
ceramics[b]	$10^{-3}-10^{-5}$
nickel-base alloys	$10^{-3}-10^{-5}$
tool steels	$10^{-4}-10^{-5}$
cobalt-base alloys	$10^{-5}-10^{-6}$
cermets[c]	$10^{-5}-10^{-7}$

[a] Based on pin-on-disk test (30).

[b] Al_2O_3, ZrO_2, SiC.

[c] WC–Co; TiC–Ni–Mo; Cr_3C_2–NiCr:Al_2O_3–CrMo.

Ceramics (qv) such as those in Table 12 find high temperature use to over 800°C (32). Advanced ceramics finding interest include alumina, partially stabilized zirconia, silicon nitride, boron nitride, silicon carbide, boron carbide, titanium diboride, titanium carbide, and sialon (Si–Al–O–N) (33) (see ADVANCED CERAMICS, STRUCTURAL).

Table 12. Typical Properties of Engineering Ceramics[a]

	Silicon carbide, hot pressed	Alumina, dense sintered	Boron nitride, hot pressed	Silicon nitride, hot pressed	Boron carbide, hot pressed
CAS Registry Number	*[409-21-2]*	*[1344-28-1]*	*[10043-11-5]*	*[12033-89-5]*	*[12075-36-4]*
max use temp, °C	1850	1700	1650	1430	1100
hardness, Knoop	2500	2500		2200	2800
flexural strength, MN/m^2[b]					
20°C	760	330		900	300
1230°C	550	145–300		310	
elastic modulus, GN/m^2[b]	420	340	50	310	450

[a] Ref. 32.

[b] To convert MN/m^2 to psi, multiply by 145.

Desirable bearing material properties offered by ceramics are high compressive strength, fatigue resistance, corrosion resistance, low density, and retention of mechanical properties at elevated temperatures. Drawbacks include low fracture resistance, and difficulty in processing and fabrication. Use of nickel, cobalt, molybdenum, or chromium is often desirable for bonding ceramics in bearing materials to provide increased toughness, ductility, and shock resistance. *In situ* solid lubricant coatings, such as graphite intercalated with $NiCl_2$, have been useful for providing reduced sliding friction and lower wear with alumina and silicon nitride (34).

Plasma-sprayed, flame-plated, or electrolytically deposited coatings of powders of Al_2O_3, Cr_2O_3, TiN, WC, and TiO_2 can be applied as wear-resistant ceramics on metal substrates with or without Co, Ni, or Cr incorporated to improve mechanical properties. Silver, barium fluoride–calcium fluoride, and other modifying materials have also been found useful in ceramic coatings for improved friction and wear properties (35). Diamond coatings are also being developed (36).

Rolling Bearing Materials

Ball- and roller-bearing materials are commonly selected to provide a minimum Rockwell hardness of 58–60 R_c at load-carrying contacts (37,38). Below this level, fatigue strength drops so rapidly as to seriously impair the utility of a material for rolling bearings which involve contact stresses in the 700–2800 MPa (100,000–400,000 psi) range (39).

Representative bearing steels are listed in Table 13. Ball bearings are almost exclusively made with through-hardened materials such as the industry standard 52100 and stainless 440C. Case-hardened steels, commonly containing a lower carbon content of about 0.20%, are used for the rollers and races in many roller bearings for automobiles and railroad equipment to obtain better resistance both to shock load and to cracking with heavy interference fits during mounting on shafts.

Table 13. Representative Steels for Rolling Element Bearings

Material	Nominal composition, wt %[a]						Approx. max temp, °C
	C	Cr	Mn	Si	Mo	Ni	
Through-hardened							
AISI 52100 *[12725-40-5]*	1.0	1.5	0.35	0.30			150
AISI 440C *[12725-30-3]*	1.0	17.0	0.48	0.41	0.75		175
MHT[b]	1.0	1.5	0.35	0.35			260
Case hardened							
AISI 1570	0.70		0.95				150
AISI 4620	0.20		0.55		0.25	1.8	150
AISI 4820 *[35724-97-5]*	0.20		0.6		0.25	3.5	150
AISI 8620 *[12731-87-2]*	0.20	0.50	0.8		0.20	0.55	150
AISI 3310	0.10	1.6	0.50			3.5	175
CBS-600	0.19	1.0	0.60	1.1	1.0		205
CBS-1000[c]	0.20	1.0	0.50	0.5	5.0		315
Tool steel[d]							
M-50 *[12725-39-2]*	0.80	4.0	0.30	0.25	4.2		350
T-1 *[37241-62-6]*[f]	0.70	4.0	0.30	0.25			450
M-1 *[12611-88-0]*[f]	0.80	4.0	0.30	0.30	8.0		480

[a] Balance iron.

[b] Also 1.4% Al.
[c] And 0.9% V.
[d] All tool steel has 1.0% V.
[e] And 18% W.
[f] And 1.5% W.

With their more ductile core, these steels are carburized to give a case hardness of 58–63 R_c to a sufficient depth to accommodate the high rolling contact stress within the higher fatigue strength of the case-hardened material (40). Many automotive front wheel drive bearings now use 52100 through-hardened steel and case-hardening alloys such as 1570. Large rolling bearings for supporting excavators, cranes, etc, employ heat-treatable steel of increased alloy content and 0.4–0.5% carbon. Their raceway surfaces are frequently gas carburized or induction hardened (41).

Vacuum melting procedures are employed in producing bearing steels to minimize oxides, other nonmetallic inclusions, trapped gases, and trace elements present in conventional structural alloys (42). With these cleaner steels and improved refining techniques providing fewer initiation sites for fatigue cracking, fatigue life improvement can range up to 3–20 times the values reflected in traditional catalog ratings for air-melted 52100 and other bearing steels.

Typical drop in hardness with rising temperature for representative steels is shown in Figure 2. The operating temperature limit for AISI 52100 steel bearings commonly ranges from 125 to 175°C. When operating temperatures exceed this range and approach the final steel stabilizing temperature, the small amount of retained austenite *[16263-38-0]* phase may transform to less dense martensite *[12173-93-2]* with an increase in bearing dimensions. Case-carburized bearings also are generally limited to an upper operating temperature of 150–175°C.

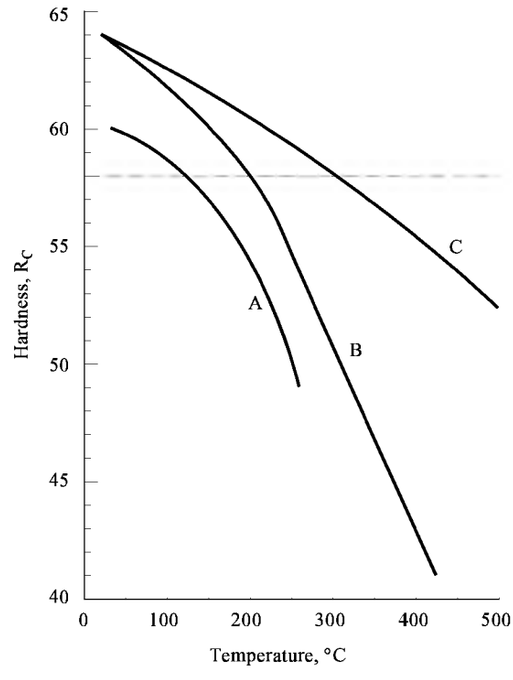

Fig. 2. Hot hardness of representative steels for rolling element bearings. A, AISI 4620; B, AISI 52100; C, tool steel M-50 (see Table 13) (39).

Tool steels listed in Table 13 are commonly used for temperatures above 175°C where hot hardness is required. M50 tool steel has been widely used, for instance, for the severe conditions encountered in aircraft jet engine bearings (42). Figure 2 shows the superior hot hardness of M50 as compared with traditional through-hardened 52100 and case-hardened 4620 steels (39).

Ceramic materials, and especially Si_3N_4 silicon nitride *[12033-89-5]*, are being applied in a variety of demanding applications. Unique properties which continue to bring them into significant development programs include: (*1*) low density of about one-half that of steel which dramatically reduces the troublesome centrifugal self-loading by steel balls and rollers at 50,000 rpm and even higher speeds in aerospace units and machine tools (38); (*2*) low coefficient of expansion which reduces loss of internal clearance in a bearing during severe temperature gradients; (*3*) high temperature capability with essentially elastic behavior at temperatures up to 1000°C and above, which enables high temperature use with solid lubricants such as tungsten sulfide *[39474-11-8]* (WS) or molybdenum disulfide *[1317-33-5]* (MoS_2); and (*4*) inert chemical characteristics which enable survival in hostile environments which would corrode steel (42). Additives of tungsten carbide *[12070-13-2]* (W_2C) and other metal oxides and carbides are useful in reducing ceramic wear (43).

Ceramic ball bearings are also sometimes effective in operation with water which would result in rapid failure with steel bearings. This capability may result from a thin hydrodynamic film formed from very small hydrated Si_3N_4 wear particles and the water (44).

Hybrid bearings using Si_3N_4 ceramic balls with M-50 or other tool steel rings enable operation up to 300°C while avoiding the difficult manufacturing problems with ceramic rings (45).

Most ball and roller bearings use a retainer, also called a cage or separator, to properly space the balls or rollers between the stationary and rotating rings of the bearing. Since stresses on the retainer are normally low, low carbon strip steel has commonly been selected for simple manufacture at low cost. In the past, many roller bearings used leaded bronze or aluminum bronze. The aerospace industry has used steel and iron–silicon bronze cages, often with sacrificial silver plating to enable operation during periods of marginal lubrication. A variety of alloys used for retainers are listed in Table 14.

Table 14. Rolling-Element Bearing Retainer Materials

		Nominal chemical composition, wt% [a]							
Material	CAS Registry Number	C	Mn	P	Si	Ni	Cr	Cu	Zn
Ni-Resist 3		2.60	0.6	0.20	1.70	30.0	1.40	0.50[b]	
S Monel[c]		0.1	0.8		4.0	bal			29.5
iron–silicon–bronze[d]			1.0		3.0			bal	3.0

bronze[e]								65.0	34.0
AISI 1010[f]	*[12725-33-6]*	0.13	0.45	0.04					
K Monel[g]	*[11105-28-5]*					bal		28	
brass	*[12597-71-6]*							65.0	35.0
AISI 304	*[11109-50-5]*	0.08	2.0		1.0	10.0	19.0		
AISI 430	*[11109-52-7]*	0.12	1.0		1.0	0.50	16.0		
Grade L			phenolic resin laminate						
H Monel[c]			0.75		3.0	63.0		31.0	

[a] Balance is Fe unless otherwise noted.

[b] Maximum amount.

[c] 2% Fe.

[d] 1% Fe.

[e] And 1% Sn.

[f] And 0.05% S.

[g] Combination of Fe and Zn, 5.0% maximum.

A continuing trend has been to polymeric retainers. Laminated phenolic cages have often been used for high speeds at temperatures up to 130°C. Heat stabilized nylon-6,6 has come into broad use in small ball bearings, both with and without glass reinforcement (39). Polyimide and PTFE are used up to 250°C.

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BEER

Beer is generally defined as an alcoholic beverage made by fermentation of a farinaceous extract that is obtained from a starchy raw material, barley, in the form of malt. Although it is possible to replace some part of the barley with other starchy materials (eg, corn, rice, wheat, oats, or potatoes), it is usually the main constituent of brewing materials. Between the ripe barley and the refreshing glass of beer, there are many production steps involving some of the most difficult disciplines of biochemical and physical science. Despite all the scientific knowledge developed in the last century, some brewing information remains culturally derived.

The making of alcoholic beverages is nearly as old as civilization. Wherever any form of culture was established, people discovered how to make some type of fermented drink, and in earlier stages always from some naturally found sugar-containing material, such as the agave juice of Mexico, the juice of the sugar maple, the juice of grapes, or honey from wild bees. The making of beer demanded a higher form of culture, however, since people had to establish a form of agriculture and produce some sort of grain (1).

Barley and emmer were undoubtedly employed in the preparation of fermented liquors long before the dawn of recorded history, especially in places where they were the chief cereals used for food. Beer is known to have been widely used as a drink in ancient Egypt and has been traced back to the age of the pyramids, some four to five millennia BC, but recent investigations suggest that the Egyptians learned the art of making beer from the peoples of the Tigris and Euphrates valleys, where beer played a large part in the domestic economy 5000–7000 BC. Barley was the predominant cereal of the ancient world, the basis of barter and exchange in Chaldea, 3000–5000 BC, and when displaced by spelt for bread making (see BAKERY PROCESSES AND LEAVENING AGENTS), it still retained its preeminence as the raw material of brewing and has continued to do so except in countries where the abundance of rice placed that cereal in an unassailable position as the source of the national fermented beverage. The use of barley for brewing is not, however, based on traditional usage alone. It has technical advantages that place it above all other cereals for that purpose. Barley differs from the other common cereals in that the husk adheres to the kernel after threshing, as it does in spelt. This renders the processes of malting and subsequent extraction of the fermentable products much easier than with wheat or other grains. Barley grows well in countries where the vine, rice, or palm cannot be cultivated. Since it is a storehouse of starch that can be converted readily and naturally to fermentable sugars, together with proteins and other valuable constituents, it is the logical source material for the national beverage of these countries (see BEVERAGE SPIRITS, DISTILLED; FERMENTATION; WINE).

During the Middle Ages in Europe the art of brewing was preserved in the monasteries. The first industrialization of beer brewing was in the large and prosperous Hanseatic cities of northern Germany and Flanders. The modern brewing industry in continental Europe originated in Bavaria.

The Anglo-Saxon invaders introduced the art to Great Britain, and as Tacitus stated, "For drink they use the liquid distilled from barley or wheat after fermentation has given it a certain resemblance to wine." As early as 1295 AD, the abbots of Burton-on-Trent used the local water which is especially suited for brewing ale and beer.

The Indians in the Americas knew about beer long before the Europeans settled there (2,3). The South American Indians brewed a variety of starch-containing plants, eg, batate, corn, yams, peanuts, banana, and manioca.

In the past century, the brewing industry has been using scientific research in order to carry out brewing with increased proficiency and confidence. Louis Pasteur of France (4) and Emil Chr. Hansen of Denmark did much to elucidate the mysteries of fermentation.

The word beer originally comes from the Latin verb bibere, meaning to drink. Today the Germans call it bier, the French bière, the Italians birra, and the Japanese biru. In Spain and Latin America, however, a different Latin root led to the modern word cerveza. This began as cerevisia, which some philologists say combines the Latin Ceres, goddess of grain, and vis, vigour. In Old High Scandinavian, the word for beer was alu, which has now been changed to the modern Scandinavian øl, in Latvia allus, Estonia õllet, and Finland olut. In Old Anglo-Saxon the name was eale, which has changed to today's ale (5).

Types of Beer

A complete survey of the different types of beer with which one might be confronted during a worldwide trip is almost impossible. Various conditions such as tradition, taxation, and other peculiarities have resulted in the beer market of today, ie, numerous types varying in strength, color, alcohol content, and bitterness.

Since the 1960s the overall number of types has been decreasing, or at least remained unchanged (standard products), but some figures indicate that in the future the creation of new products might take place as a strong alternative to the previous mass-produced beers of less body or character. A traditional and overall grouping of beer can nevertheless still be made, ie, bottom-fermented beer and top-fermented beer.

BOTTOM-FERMENTED BEERS

Pilsner. Pilsner is a pale beer with a medium hoppy taste. It contains 3.9–4.7% by vol alcohol and is traditionally lagered 2–3 months. The water for this type of beer is soft and contains a small amount of salt. Some 70–80% of all beer consumed in the world is of this light-lager type.

Dortmund. Dortmund is a pale beer with fewer hops than Pilsner but more body and taste. The alcohol content is 3.9–4.7% by vol and storage time is 3–4 months. The brewing water is hard and contains large amounts of carbonates, sulfates, and chlorides.

Munich Beers. Munich beers are dark brown with a full-bodied, slightly sweet taste. They are only mildly hopped. The alcohol content is 3.2–6.3% by vol and storage time is 3–5 months. The brewing water has many carbonates but only small amounts of other salts. Bock, Salvator, and Würzburger beers are Munich-type beers. Bock beer, a seasonal beverage made with caramelized or highly roasted malts, is traditionally brewed in the winter for spring consumption, as it is too satiating for year-round consumption.

TOP-FERMENTED BEERS

Ale. Ale is pale with a pronounced hop taste and aroma, and 5.1–5.7% by vol alcohol. In Burton-on-Trent, England, where the best ales are made, the brewing water is rich in calcium sulfate; elsewhere it is usual to burtonize the water by adding calcium sulfate. In addition to the amount of hops used in the brewing, more dry hops are added during storage in order to have a distinct hop aroma in the finished product. There are two kinds of ale: pale (bitter) and mild. Bitter ale is strongly hopped and has a dry taste whereas mild ale is sweeter tasting. The famous English half-and-half is half bitter and half mild ale.

Porter. Porter is a dark brown, full-bodied beer with a heavy foam. It is less hoppy and slightly sweeter in taste than ale; it contains 6.3% vol alcohol and is made with some dark or black malts.

Stout. Stout is a very dark beer with a sweet, slightly burned taste and a strong malt flavor. It is heavier than porter and is strongly, hopped. It contains 6.3–8.3% by vol alcohol. Storage time is about six months and fermentation usually occurs in the bottle. Dry and sweet stouts are brewed using different amounts of black malt, caramel malt, and hops (6).

Lambic Beer. Lambic beer is made in Brussels and is one of the few top-fermented beers still brewed in Belgium. It is made from 60% barley

malt and 40% unmalted wheat. The beer is strongly hopped and fermentation is spontaneous with wild yeasts, lactic acid bacteria, and bretanomyces. Fermentation and storage take place in the same vats and the beer is kept there for two or more years.

Others. The only top-fermented beer in Scandinavia is Hvidt Øl; it has a low alcohol content (2.6% vol), a high level of extract, and is very mildly hopped. Smoke Beer is manufactured in Germany and Denmark. It is made entirely from malt that is dried by direct beechwood fumes. In Denmark it is called Skibs Øl (Ships Beer) and for centuries was intended for consumption in the Danish Navy and Marines since it had better keeping qualities than the ordinary beers. It is top-fermented with low alcoholic content.

LOW ALCOHOL BEERS

During prohibition in the 1930s, the United States tried to make beers with a low alcohol content. In later years, further attempts were made in other countries to create such beers because of the need for stronger measures against alcohol abuse by drunken drivers. The difficulty in making a beer with low alcohol content and a low degree of fermentation is its pronounced wort taste. The following measures can be used in making such beers: interruption of the fermenting process; scalding beer in the copper kettle; vacuum distillation; or reverse osmosis.

There are drawbacks to each one of these procedures. Because the beer aroma is formed during fermentation the low alcohol beers obtained by interrupting the fermentation lack a strong aroma. By scalding normal beer the aroma substances that are already formed will evaporate as well as the alcohol. An improved beer quality has been obtained during recent years by using the modern and more advanced filtration techniques based on more and more sophisticated membrane-flux characteristics. By using the right membrane, pressure, and time it is possible to reduce the alcohol content of beer to lower levels with minimum flavor loss.

A beer with normal alcohol content, but much lower in caloric content, can be made with the help of external, specific enzymes that are added during mashing or fermentation to achieve further breakdown of carbohydrates.

Properties of Beer

The properties of the finished beer vary with the type of beer and place of origin. The figures in Table 1 do not, however, show much about the quality of the beer; this can only partly be expressed in figures based on objective measurements. The quality consists of aroma, taste, appearance, (color, clarity) formation, and stability of foam. Of these, the first two are still inaccessible to objective measurement. Although the aroma of a product is determined by the quantity of volatile alcohols, etc, the quality of the product cannot be expressed in those terms. Appearance, foam formation, and foam stability can be evaluated more easily. For judgment on taste and aroma, taste-testing panels are the only method.

Table 1. Properties of Beer[a]

Property	Pilsner Urquell[b]	U.S. lager	Danish pilsner	English ale	English stout	Munich Löwenbrau	Dortmund
original wort extract, °P[c]	12.1	11.5–12.0	10.6	15.0	21.1	13.3	13.6
real extract content, °P[c]	5.3	5.5	3.1	5.0	8.7	6.4	5.5
alcohol content, vol %	4.4	4.3–4.7	4.7	6.6	7.2	4.4	3.8
protein content, wt %		0.28–0.35	0.3	0.6	0.8	0.5	0.6
CO_2 content, wt %		0.53	0.50	0.40	0.41		0.42
color, EBC[d]	10	2.7	5			40	8
air in bottle, mL		1.5	2	8	10		6
pH		4.25–4.50	4				
real degree of attenuation, %		60–75	69	66	59	48	60

[a] Ref. 7.

[b] Urquell is a trade name belonging to Bürgerliches Brauhaus in Pilsen, Czechoslovakia.

[c] °P = °Plato, wt % extract (sugar).

[d] EBC = European Brewery Convention.

Nutritional Value of Beer. The importance of beer as a nutrient has been examined since 1950. Beer is drunk primarily as a source of liquid and for its pleasant and refreshing taste; nonetheless, its nutritional properties are of great importance. The caloric content of beer is significant but not especially high. A 355 mL (12 oz) bottle of average beer (about 10.7°P = 1.045 original gravity) yields approximately 560 kJ (135 kcal). Normal daily total dietary intake is ca 10,000 kJ (2400 kcal). The calories in beer are provided by the unfermented residues and by the alcohol. The metabolic role of the latter is not fully understood but it replaces carbohydrates, fats, and proteins so that there may be a gain in body weight. Besides its caloric value, beer also contributes to the mineral requirements of the body (Table 2) and supplies useful quantities of B-complex vitamins (see VITAMINS).

Table 2. Mineral Content of a Normal, Light, 11.5°P[a] Beer from Switzerland in mg/L

total ash	1.754
silicon	58
calcium	21
magnesium	94
potash	458
sodium	125
iron	0.4
copper	0.3
aluminum	0.3
cobalt	0.01
sulfate	154
phosphate	675
chloride	149

[a] °P = °Plato, wt % extract (sugar).

A special use of beer is for the control of sodium intake in the treatment of diseases such as congestive heart failure, high blood pressure, and certain kidney and liver ailments. Because of its low pH (ca 4.2), beer cannot harbor any pathogenic germs. The content of nourishing components are all in dissolved form. Beer is free from fat, it acts as a diuretic (see DIURETICS), and it promotes the formation of gastric acid, acting as an appetite inducer.

The effect of consuming alcohol on human behavior and reactions is well known, but the effect is somewhat less severe from beer compared to

"hard liquor," ie, whiskey and gin, because of the lower alcohol content and, normally, a completely different drinking pattern or speed of consumption (Fig. 1).

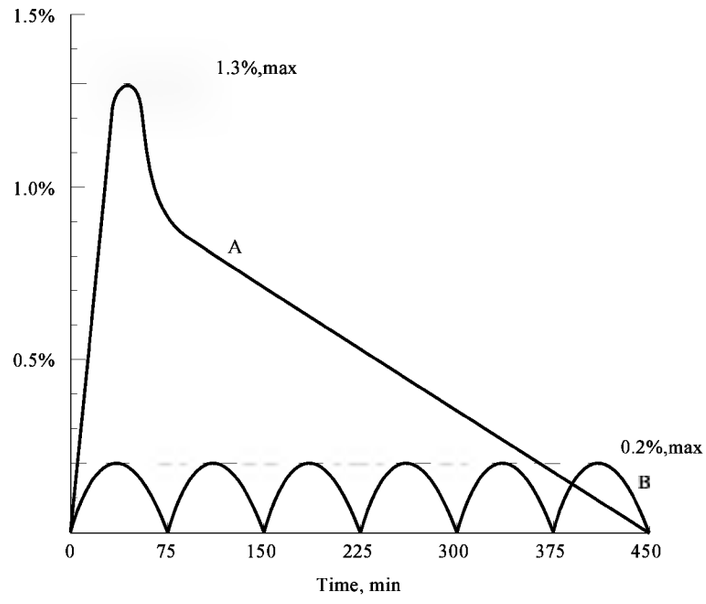


Fig. 1. Blood alcohol concentration after consumption of an equal quantity of alcohol in two different ways. A, three double Martinis within 30 min; B, six beers (12°P) within an interval of 75 min.

Beer Defects. Among beer defects turbidity or haze is of primary importance. It may be either biological or physicochemical in nature. The former occurs only in unpasteurized beer and is caused by growth of microorganisms, such as brewers yeast, wild yeast, or certain bacteria. The latter may be induced by oxidation, metals, chilling, and heating (pasteurization). Chill haze is rich in sulfur (1.8–2.0%) indicating a rather high content of active sulfhydryl groups (–SH) that are readily subject to oxidation. When oxidation occurs, sulfur to sulfur linkages (–S–S–) are formed in proteins. The oxidized compounds are insoluble, thus producing an oxidation haze with its consequent deleterious effect on the flavor and shelf life of the beer. Complexation of tannins and proteins may also occur.

In a modern brewery the importance of oxygen and traces of metals is no longer a problem as far as haze-stability is concerned. On the other hand, oxygen is still of importance in considering taste and taste stability, because oxidized beers have a distinct cardboard flavor correlated to the amount of *trans*-2-nonenal *[18829-56-6]*, C_9H_1 O, present in the beer (0.5–1.0 pbb). Modern analysis techniques have made it possible to measure the oxygen content in head-space volume as well as in solution in the beer, and it is the total amount of oxygen that counts. This knowledge speeded up improvements of filling machines and filtration techniques, and consequently taste stability improved considerably.

The effect of sunlight, ie, the sunstruck flavor in beer, is caused by the formation of mercaptans. The portion of sunlight that is photochemically active is the blue-green region of the visible spectrum (420–520 nm).

Wild or gushing beer is a defect observed as a rather violent over-foaming from the bottle immediately after opening. This defect, however, does not affect the taste of the beer, but it is the most disastrous and complex problem a brewery might experience. Some reasons for gushing have been cured or removed, but others must be addressed before the gushing problem is fully under control. The most prevailing theory, which has been demonstrated experimentally, says that metabolic products from certain mold species of *Fusarium* and *Aspergillus*, developed on withered barley not sufficiently dried before storage, is the main reason for gushing. Even though the mechanism is not yet understood, this theory explains why some beers suffer from gushing disease. But the same beer may not gush equally in all bottles, ie, in new and one-way bottles less than in old returnable bottles. Consequently, it is obvious that other relations must play an important role in the total picture of the gushing problem. Another theory suggests that the surface of the bottles might be decomposed by different cleaning solutions, and thereby transformed to centers for CO_2-bubble formation. Because it is almost impossible to differentiate between the various species within the *Fusarium* and *Aspergillus* families, and only a few are really dangerous, it is very difficult to handle gushing in practice. Presently the problem is addressed by the long and time-consuming method of making trial brews in small scale of all new barley-malt deliveries in question, and analyzing the gushing potential in the trial-beers. This effort indicates whether the malt might cause gushing problems or not and whether it should be blacklisted or only used in smaller percentages.

Brewing Materials

Barley. Barley is the predominant raw material of beer in most countries, except where other cereals are cultivated, eg, rice in China and kafir in Africa. Barley has technical advantages that make it superior for malting and brewing (8). It differs from the other common cereals in that the husk adheres to the kernel after threshing, making malting and subsequent extraction of the wort much easier than with wheat or other grains. Barley grows well in countries where vines, rice, or palm cannot be cultivated. Because it contains starch proteins and other valuable constituents (Table 3), it is the logical source material for brewing (9).

Table 3. General Analysis of Barleys[a]

	Two-row, %	Six-row, %
starch	60	52
sugars	2.5	2.5
hemicelluloses, pectins, etc	8	11
cellulose	4	7
lignin	1.5	3
protein and other nitrogenous substances	9	9
fat	2.5	2.5
ash	2.5	3
tannin	small quantity	small quantity
water	10	10

[a] Ref. 9.

Barley may have either two or six rows of fertile kernels, and, because it differs in so many other qualities, there are several thousand varieties. European breweries almost exclusively use two-row barleys; six-row barleys are predominant in the United States. The two-row barleys are richer in extract than the six-row. However, the latter is richer in enzymes which are important when large amounts of adjuncts are being used.

During the malting process the raw, hard, flat-tasting barley is changed into a crisp, mellow, sweet-tasting malt. The germ is only a small part of the barley kernel; the rest is a proteinaceous cell tissue filled with starch. However, starch and proteins are not directly soluble in water. The aim of malting is to bring forth enzymes, that will hydrolyze starch and proteins to less complex, water-soluble compounds, ie, amino acids, fermentable sugars, and small peptides. When these compounds are dissolved in water the resulting liquid is known as wort.

Brewers are especially interested in the starch-splitting amylases. They are formed in barley during germination, but react mainly during mashing. The protein-splitting enzymes, proteases, are formed and react during germination so that some of the proteins of the barley are split into compounds soluble in water. The hemicellulases, another group of enzymes, split the cell tissue thereby leaving the starch open to attack by amylases.

The character of the malt plays a large role in the resulting beer (Table 4). The two extremes in malt character are reflected in Pilsner and Munich beers. For Pilsner, a pale malt with no pronounced aroma must be used; the drying of the malt takes 20–24 h at 80–90°C. Munich beer demands malts with a pronounced aroma; in this case the drying takes up to 48 h at 100–110°C. Although the water content of the final malt is 3–4% , the interplay of water content and temperature during the drying is of fundamental importance for the character of the malt. The pale malt must be quickly dried to reach the final temperature; the dark malt must have a suitable high water content as the temperature rises. Special malts, such as caramel and black, are used for the darkest beers, such as porter and stout. These malts have pronounced color and aroma but little or no diastatic power (see MALTS AND MALTING).

Table 4. Analysis of Malts[a]

			Danish		
	Pilsner	Munich	Pilsner	Munich	English
moisture, %	6.1	4.2	3.8	2.1	3.5
extract, °P[b]	78.0	77.0	79.7	79.2	82.6
color, °EBC[c]	2	11–14	3	10	2
diastatic activity, W-K[d]	300	90	200	110	230
protein, % on dry matter	11.4	11.4	10.1	11.1	9.0
protein, soluble % on dry matter	4.2	3.8			
protein, permanently soluble, % on dry matter	37.3	33.0	37.5	36.0	40.2

[a] Ref. 7.

[b] °P °Plato, wt % extract (sugar).

[c] EBC European Brewery Convention.

[d] Windisch-Kolbach units, named for two German brewing scientists.

New techniques, ie, genetic engineering or genetic manipulation, have been used in the field of barley improvement. The most interesting result has been a barley variety with little or no content of the tannin fraction called proanthocyanogen in the husks. This barley opens new possibilities for controlling the haze stability problems mentioned earlier. Other desired and more rapid improvements of barley characteristics from a cultivating and brewing point of view can be foreseen in the future by using this technique.

Adjuncts. Adjuncts in the form of cereals other than barley are often part of the brewing materials when the demand is for a stable, nonsatiating, sparkling beer. Since barley malt usually contains more enzymes than are necessary, the malt is mixed with unmalted, starchy material. Sugar can be added during various steps of the brewing instead of forming fermentable sugar through the splitting of starch during mashing. Since adjuncts are essentially starch with very little protein, they are a source of additional alcohol but contribute little to the color, taste, aroma, or protein content of the beer.

Corn (*Zea maize*), the greatest source of cereal adjuncts, is milled in two ways: wet or dry. Milling removes most of the germ and husk containing <7% of fatty oil. Refined grits, obtained from the wet milling, are the highest yielding and purest cereal adjunct. Corn grits, obtained by dry milling, are the most commonly used adjunct. Rice can be used with, or instead of, corn grits, depending on availability and price. Milo grits (sorghum) and cassava (manioc) have proved to be acceptable substitutes during grain shortages. Wheat, unmalted barley, and potato starch have been used only in limited amounts and with limited success. Brewing sugars and syrups are excellent brewing materials when properly prepared and free from iron. Soybeans containing rather large amounts of various B vitamins are often added in small amounts because they appear to aid in the nourishment of the yeast and improve the fermentation. Besides the qualitative aspect, the use of adjuncts has an economic advantage in that the various unmalted cereals are usually cheaper than barley malt (10).

Hops. Hops are the blossoms of the female hop plant, wild in North and Middle Europe, North Asia, and North America. The composition of hops is shown in Table 5 (see also ref. 11).

Table 5. Composition of Hops[a]

Component	Wt %
water	12.5
ash	7.5
raw cellulose	13.3
proteins	17.5
volatile oil	0.4
ether extract, mostly resins[b]	18.3
tannin	3.0
protein-free extract substances	27.5

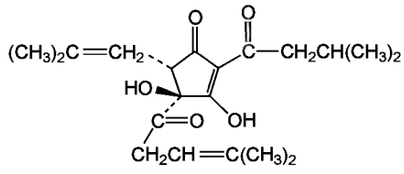
[a] Ref. 7.

[b] See Table 6.

Originally the principal aim of adding hops was to compensate for the insipid, sweet taste of the unhopped beer with the characteristic bitter taste and aroma of hops. Other assets of adding hops include increasing the biological stability of the beer and improving the head retention and body of the beer. The amount of hops added varies from 0.4–4.0 g L. In the original Pilsner beer, the amount is about 4 g L but elsewhere much smaller amounts are used.

By far the most important constituents of hops are the bitter substances, humulones (α-acids), lupulones (β-acids), and their oxidation products,

hard and soft resins (Table 6) (Fig. 2). A correlation between the bittering power of the hops and the bitterness of beer has yet to be found. Research has shown that α-acids are transformed into iso-αacids during boiling; however, their output is deficient and irregular. Examples of iso-α-acids include *cis*-isohumulone *[1534-03-8]*, (7), and *trans*-isohumulone *[467-72-1]*, (8).



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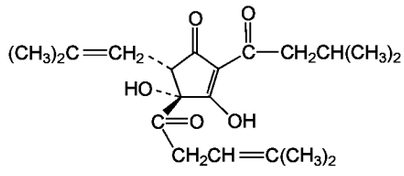

(8)

The use of hops in the form of hop extract has spread rapidly; the yield of the extract is better, yet insufficient. The production of a satisfactory hop extract quality, ie, no taste difference to beer hopped by using other "natural" hop products, has appeared to be a science or art in itself. Use of the right solvent and distillation is the key point, and many unsuccessful attempts have been made. The latest and most successful method, using the so-called liquid carbon dioxide extraction, meets the high quality demands almost perfectly. Preisomerization of the resins makes it unnecessary to boil them with the wort; they can be added directly to the finished beer to avoid poor yield (through boiling) and the loss of resins (during fermentation).

Table 6. Hop α-Acids (Humulones) and β-Acids (Lupulones)[a]

R group[b]	Name	CAS Registry Number	Molecular formula	Structure number
α-Acids				
$(CH_3)_2CHCH_2$	humulone[c]	*[26472-41-3]*	$C_{21}H_{30}O_5$	(**1**)
		[23510-81-8]		(**2**)
$(CH_3)_2CH$—	cohumulone	*[511-25-1]*	$C_{20}H_{28}O_5$	(**3**)
				(**2**)
	adhumulone	*[71800-99-2]*	$C_{21}H_{30}O_5$	aa
CH_3 CH— CH_3CH_2		*[31769-65-0]* *[28374-89-2]*		
$(CH_3)_2CHCH_2CH_2$	prehumulone		$C_{22}H_{32}O_5$	a
β-Acids				
$(CH_3)_2CHCH_2$—	lupulone[d]	*[468-28-0]*	$C_{21}H_{38}O_4$	(**4**)
$(CH_3)_2CH$—	colupulone	*[468-27-9]*	$C_{24}H_{38}O_4$	(**4**)
	adlupulone	*[31769-60-5]*	$C_{21}H_{38}O_4$	(**5**)(**6**)
CH_3 CH— CH_3CH_2		*[28374-71-2]*		
$(CH_3)_2CHCH_2CH_2$—	prelupulone		$C_{28}H_{40}O_4$	a

[a] Hop "bitter" acids are isomeric mixtures of cyclohexadienone structures in both keto and enol forms, substituted at various positions on the ring by hydroxyl, acyl, and alkenyl groups. See Figure 2.

[b] Of the acyl substituent.

[c] α-Lupilic acid.

[d] β-Lupilic acid.

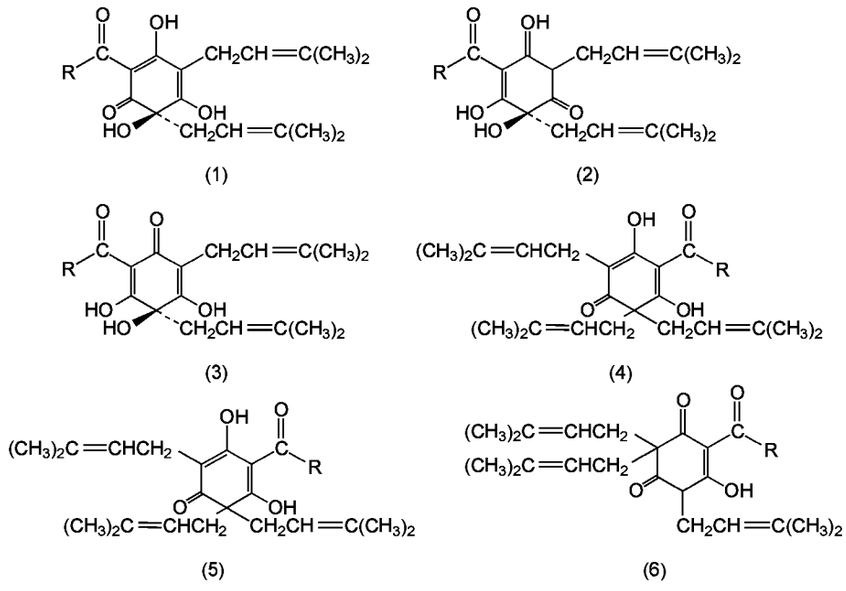

Fig. 2. Representative structures of α- and β-hop acids. R groups are defined in Table 6.

Brewers Yeast. Yeast for brewing is originally propagated from single-cell cultures and is recovered after fermentation for use throughout several generations. There are two types of yeast in brewing: top yeast, which forms spores, ferments vigorously at elevated temperatures, and tends to float on top of the beer; and bottom yeast, which does not usually form spores, is well adapted to slow fermentation at low temperatures, and settles to the bottom of the tank at the end of fermentation (12) (see YEASTS).

There are two types of bottom-fermenting yeasts named after the weakly attenuating Saaz and the strongly attenuating Frohberg yeasts. The former flocculate readily and are known as break yeasts, whereas the latter, dusty or powdery yeasts, remain suspended in the worts. The latter are preferred for beers that must be fully attenuated and very stable in trade. Brewery yeasts have generally all been regarded as varieties or strains of *Saccharomyces cerevisiae.* Alternatively, top- and bottom-fermenting yeasts may be considered to be different and classified as *S. cerevisiae* and *S. carlsbergensis*, respectively. The two types may have arisen as the result of a process of selection in a yeast that originally contained both types. As a result of low fermentation temperatures used in lager breweries, certain types persisted, while others, which preferred higher temperatures, were gradually eliminated until only the former were left to form the bottom yeasts now in use. Both species include many strains that have been separated as pure strains and are hence known as culture yeasts. The characteristics of the strains of *S. carlsbergensis* (uvarum) are better known as pure cultures and are generally more often employed in bottom-fermenting breweries. Thus *Saccharomyces carlsbergensis* is considered the type of species for bottom fermenters, and certain strains of *S. cerevisiae* for the top fermenters. The physiological characteristics of the two types have been thoroughly investigated, initially because brewers and manufacturers of bakers yeast by the old Vienna process had to know whether a strain to be used in their production was a top fermenter, a bottom fermenter, or a mixture. The ability of a yeast to ferment a specific carbohydrate is often qualified with such terms as "ferments weakly" or "ferments occasionally." Although the speed of fermentation and the limiting concentration of sugar and or alcohol are usually disregarded in taxonomy, they are carefully evaluated in the practical classification of industrial strains. The fermenting of raffinose *[572-69-6]* is of great diagnostic value. Depending on the presence or absence of certain genes for the respective hydrolyzing enzymes, some yeasts cannot ferment raffinose at all, some ferment only one-third, some as much as two-thirds, and some the whole of the trisaccharide molecule. For example, *S. carlsbergensis* ferments the whole raffinose molecule, whereas *S. cerevisiae* ferments only one-third of it, being unable to hydrolyze the melibiose portion. The test is generally better suited for distinguishing *S. cerevisiae* from *S. carlsbergenesis* than for determining top or bottom fermenters (13).

Perhaps the greatest preoccupation in relation to brewing yeasts is with stability, ie, whether a strain or mixture of strains remains unchanged and uncontaminated with prolonged use, and whether the range of performance of the constant strain or mixture of strains is small enough to provide adequate constancy of beer quality despite inevitable minor variations in wort composition. Various strains of yeast have individual flavor characteristics, thus brewers yeasts are not selected solely on the basis of fermenting power, but decidedly on the flavor they give beer (14).

Development of new yeast strains through genetic manipulation techniques has shown some interesting results. Strains with, eg, beta-gluconase activity are produced and have proven satisfactory.

Water. The character of the water has a great influence on the character of the beer and the hardness of water (alkalinity) manifests itself by the extent of its reaction with the weak acids of the mash. Certain ions are harmful to brewing; nitrates slow down fermentation, iron destroys the colloidal stability of beer, and calcium ions give beer a purer flavor than magnesium or sodium ions (Table 7).

Table 7. Mineral Content of Waters Used in Brewing[a]

Place	Mineral content in ppm						
	Total solids	Ca^{2+}	Mg^{2+}	SO^{2}_{4}	NO_3	Cl	HCO_3
Milwaukee	148	34	11	20	0.8	6.6	
New York	28	6	1	8	0.5	1.0	11
St. Louis	201	22	12	77	4	10	65
Pilsen	63	9	3	3		5	37
Munich	270	71	19	18		2	283
Dublin	3	100	4	45		16	266
Copenhagen	480	114	16	62		60	347
Burton-on-Trent	1206	268	62	638	31	36	287

[a] Ref. 7.

Brewing water plays so large a role that some of the world's best known beer types, such as Pilsner, Munich, Dortmunder, and Burton Pale Ale, are special because of the properties of water used in their production.

Long before the concept of pH, influences of minerals in water were empirically demonstrated in the various methods of production of both malt and beer. Water with a large carbonate content, as found in Munich and Copenhagen, demands long-grown and highly dried malt together with slow

mashing and protracted boilings of the mash. Such waters are best suited for dark types of beer, and the original beer types of Bavaria and Denmark were dark and rather low in hop content. The water in Pilsen is poor in minerals; it is best suited for pale beer made from malt dried at low temperatures and with methods of mashing that do not favor a rise in acidity. The water in Dortmund contains both carbonates and sulfates; the sulfates counteract the alkaline effect of the carbonates so that the beers of Dortmund are also pale. The special beer at Burton-on-Trent, England, is made from a very pale malt and mashing by infusion.

When the available water is not suitable for the desired beer type, the question of water treatment arises. If the production of a pale beer with a fine hop taste is desired and the water is rich in carbonates, one of the following methods of treatment may be used: addition of gypsum (burtonizing); addition of acid; decarbonation; and demineralizing by ion exchange (qv). Addition of gypsum (calcium sulfate) neutralizes the alkalinity of the carbonates. Carbon dioxide is set free by the addition of an acid; sulfuric acid, hydrochloric acid, phosphoric acid, and lactic acid are optionally used, but differently according to the type of beer wanted. These methods are easily employed, but the salt remains in the water and this is not always desirable. Decarbonation is the removal of the carbonates, either by boiling or by the addition of lime. Until about 1940, it was not possible to improve the brewing water through ion exchange as with boiler water, since this treatment exchanges the desired Ca^{2+} and Mg^{2+} with Na^{+} but leaves behind the undesired carbonate buffer system. Today it is possible to treat brewing water through double ion-exchange, a process in which all salts are completely removed.

Production

The most important phases during brewing are mashing, wort boiling, fermenting, lagering, filtering, and bottling or keging (Fig. 3). During mashing, a mixture of finely crushed malt and warm water is exposed to enzymatic activity, thus converting starch into miscellaneous sugars and protein into peptides and amino acids. The dissolved product from mashing is called wort (15) and the insoluble remainder (mostly husks of the malt) is called spent grain, which is sold as cattle fodder. The wort is boiled with hops and, during boiling, the enzymes are destroyed while bitter substances are extracted from the hops. Boiling of the wort also causes a certain amount of unconverted protein to coagulate and flocculate. This flocculation appears in the boiled wort as flocs; the brewer says that the wort has a fine break. After separation from the wort it is called a sludge.

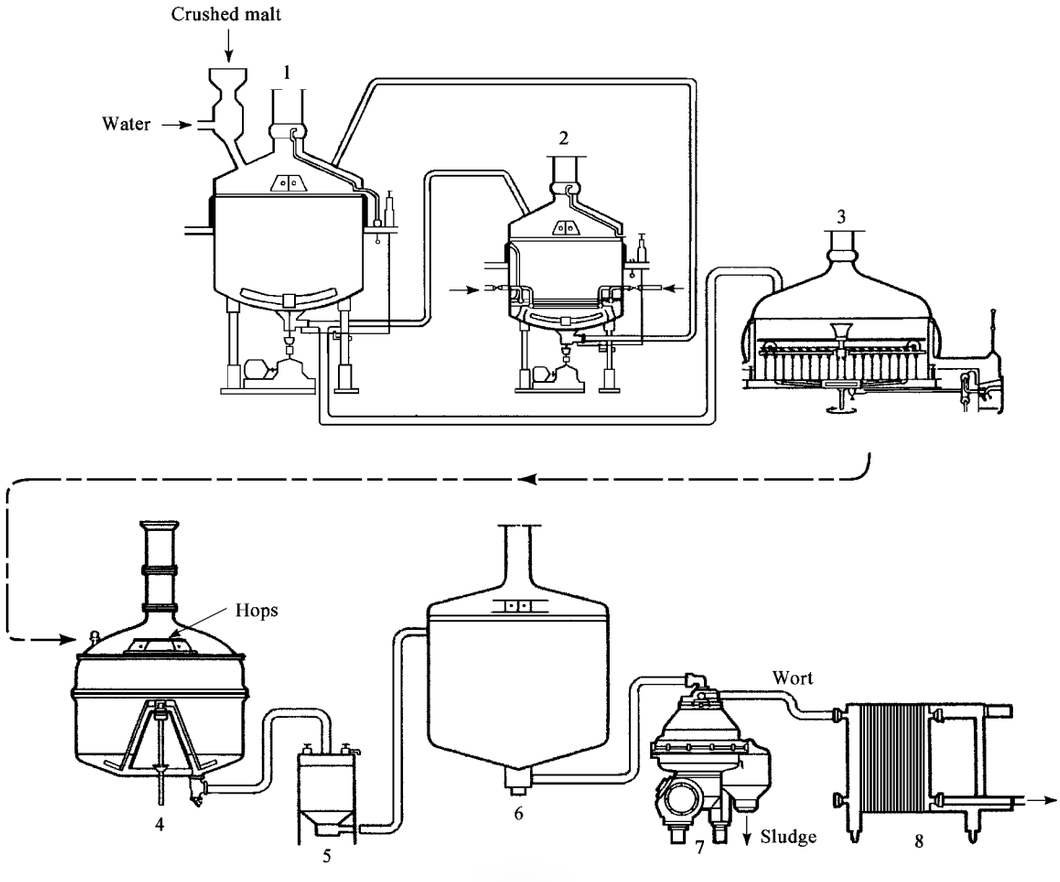

Fig. 3. Brewing (1 mash turn; 2 = mash kettle; 3 = lauter tun; 4 wort kettle; 5 hop strainer; 6 = wort tank; 7 wort separator; and, 8 wort cooler).

After cooling of the wort to about 10°C, the yeast is added in order to convert the sugar into alcohol and carbon dioxide during fermentation. After fermentation most of the yeast is harvested followed by a slow after-fermentation and maturing of the green beer in lagering tanks. By the end of the lagering there is a sediment in the tank, called draff, consisting of the remaining yeast together with precipitated proteins and tannins. During this process the temperature decreases from 5 to 1°C, or the beer may be transferred to conditioning tanks while cooling down to 1°C, and this temperature is held from two to six days.

The beer is filtered into pressure tanks and transferred to the bottling or keging machine. It is then pasteurized to avoid biological spoilage. The finished product is completed in five to six weeks for pilsner beer and six to nine weeks for the stronger beers.

Grinding of Malt. To extract the malt substances quickly and efficiently the malt must be crushed before being mixed with water. The degree of crushing depends on the method of separating the wort from the spent grains. The malt should be crushed as finely as possible for a better yield of extract. However, too much flour delays the separation, and the wort retained in the filter bed more than compensates for the gain in extract. Malt mills are available in different constructions, eg, with two or four rollers with or without shaking screens, and with six rollers with shaking screens as shown in Figure 4.

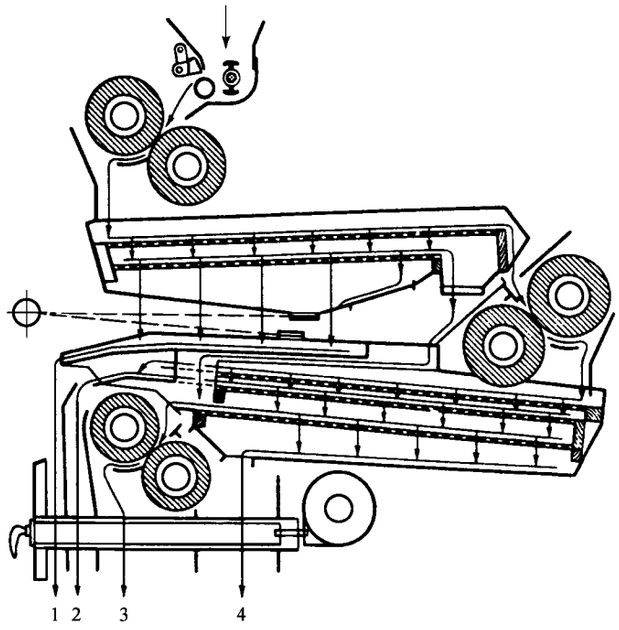

Fig. 4. Malt mill with six rollers and shaking screens (1 = flour; 2 = husks; 3 fine grits; and, 4 coarse grain).

In another process called wet grinding, the malt is soaked for a certain time and temperature, then crushed between a single pair of rollers while mixed with water and pumped to the mash tun (Fig. 5). According to the construction of the soaking system the grinding of the malt usually takes approximately one hour, and it is obvious that the condition of the first kernels is not equal to the condition of the last kernels, and subsequently the grinding result differs. In order to prevent this, a new method has been invented, ie, the so-called malt conditioning system, according to which the malt is conditioned by injecting water-steam or hot water to the malt just a few minutes before grinding. By doing this the kernels are equally conditioned, and the result is more homogeneous. The capacities of the various malt mills are from 2 to 16 t h.

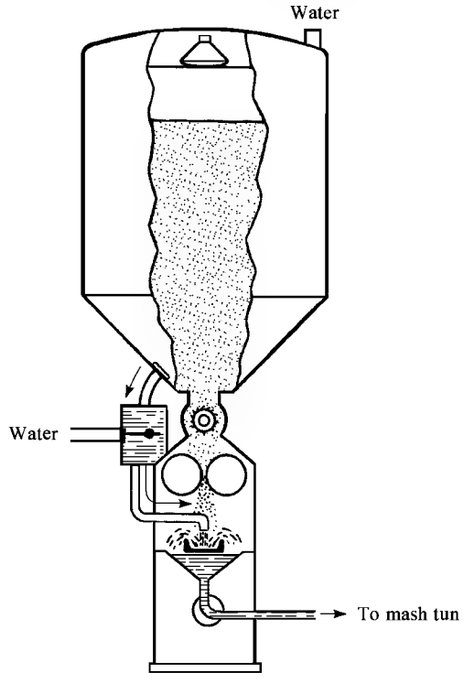

Fig. 5. Wet milling.

Treatment of Adjunct. Solid adjuncts, eg, corn grits or rice, contain high mol wt polysaccharides that are insoluble in water; they are not pretreated, ie, there is no germination or enzyme activation. Adjuncts must be treated to be accessible to attack by the malt enzymes, usually by boiling. Boiling destroys the cell walls of the adjunct with release of the starch and gel formation. If no enzymes are present,this gel has a very high viscosity. Addition of malt or malt extract before boiling (70–80°C) partially saccharifies the starch; after boiling the mixture is rather free-flowing.

Mashing. Enzymatic breakdown of polysaccharides and proteins is actually started during malting, and mashing is a continuation of this breakdown yielding the extract of the wort. It consists of dissolving water-soluble substances, enzymatic breakdown followed by solution of a series of substances important for the type and character of the beer, and separation of the undissolved substances. The breakdown during the mashing is regulated by time, temperature, pH, and concentration of the mash.

Quantitatively, the breakdown of starch to dextrin *[9004-53-9]* and maltose *[69-79-4]* is by far the most important. It takes place according to the following equations.

$$\underset{\text{(162 g starch)}}{(C_6H_{10}O_5)_n} \rightarrow \underset{\text{(162 g dextrin)}}{(n\ \ x)(C_6H_{10}O_5)_x}$$

$$(C_6H_{10}O_5)_n + (n-2)\,H_2O \rightarrow (n-2)\,(C_{12}H_{22}O_{11})$$

(162 g starch) (171 g maltose)

Starch *[9005-25-8]* constitutes about 55% of the weight of the barley kernel. Starch is a mixture of two polysaccharides, amylose *[9005-82-7]* and amylopectin *[9037-22-3]*. Amylose dominates the interior of the starch particles, whereas amylopectin is found, to a greater extent, in the outer layers. Amylose is built of glucose units bound in straight chains in such a way that the chain forms a spiral. The length of the chain is normally over 200 glucose units giving a mol wt of 36,000 or more. Amylopectin is also built of glucose units, but it is branched. The length of the straight portions between the branches is 10–18 glucose units. Amylopectin has a mol wt of 50,000–200,000. In barley, the ratio of amylose to amylopectin is about 25:75, which is normal for cereals.

During the breakdown of starch, the following four amylases are involved: α-amylase, β-amylase, (*Z*)-enzyme, and (*R*)-enzyme. Because both amylose and amylopectin are built exclusively of glucose units, it should be possible, given sufficient time and enzyme mix, to obtain glucose alone as the end product. However, intermediate products consisting of chains of glucose units with fewer links than starch appear as the breakdown advances. The carbohydrate composition of wort has been determined by chromatography (Table 8).

Table 8. Carbohydrate Composition of a Normal Wort[a]

Carbohydrate	Content[a]
monosaccharides, glucose	0.98
disaccharides, maltose	5.77
trisaccharides	1.29
tetrasaccharides	0.26
pentasaccharides	0.10
hexasaccharides	0.16
heptasaccharides	0.15
octasaccharides	0.19
nonasaccharides	0.13
higher carbohydrates	1.08
extract,	
°P[b]	10.65
g 100 mL	11.11
total carbohydrates,	
g 100 mL	10.11
% of extract	91.0
fermentable carbohydrates,	
g 100 mL	7.74
% of extract	69.7

[a] Ref. 16. Content as g 100 mL unless otherwise noted.

[b] °P = °Plato, wt % extract (sugar).

α-Amylase *[9000-90-2]* is resistant to comparatively high temperatures; its temperature optimum in the mash is 70°C and it is destroyed at 80°C. It functions best at pH 5.8. β-Amylase *[9000-91-3]* is destroyed at 75°C; its optimum operating temperature is 60–65°C in the mash and optimum pH is 5.4. Consequently, the higher the temperature of the mash, the more dextrin is formed. Long retention at 60–65°C, on the other hand, gives a wort rich in maltose. By adjusting the temperature mash cycle it is possible to regulate the fermentability of the wort since maltose is easily fermentable and dextrin is not.

The pH has a great influence on the enzymatic processes during mashing. Through water treatment it is possible to bring about shifts in pH whereby the transformations are decisively influenced. β-Amylase has a pH optimum at 5.4, α-amylase at 5.8, and the normal mash has a pH of about 5.4 during saccharification. The influence of the concentration of the mash is such that thin mash increases the yield of both extract and maltose (Table 9).

Table 9. Effect of Mash Concentration on Yield of Extract and Maltose[a]

Concentration of mash, malt:water	Extract yield, %	Fermentable extract, %
1:2.0	71.7	52.3
1:2.7	77.0	56.3
1:4.0	80.0	58.5
1:5.3	79.9	57.8

[a] Refs. 17 and 18.

The breakdown of proteins in barley (albumins, globulins, hordeins, and glutelins) starts in the malt house and continues during mashing with the aid of protolytic enzymes, such as proteases and peptidases. Protein breakdown during mashing has no pronounced temperature optimum; it takes place rather evenly during the entire mashing process up to 60°C, above which the activity of the proteases and peptidases is highly reduced. Protein breakdown is highly dependent on pH; at lower pH there is an increase in breakdown. Normally, the mash has a pH between 5.4 and 5.6. In malt about 30% of the proteins are soluble in water. After breakdown during mashing, 30–40% of the proteins go into the wort. Of the total nitrogen of the wort, about one-third is proteins and peptones, which are precipitable by tannin, and two-thirds are peptides and amino acids. The peptones contribute to the head retention of beer and the peptides to the body; however, both participate in the formation of turbidity in the finished beer. The amino acids serve as nourishment for the yeast (9).

Upon mashing, small amounts of tannin go into the solution from the malt, and later, during the boiling with hops, more tannin goes into the wort. Tannins from both barley and hops are leucoanthocyanin structures, in some cases they are derivatives of quercetin *[117-39-5]*; cathechins are not found. The turbidities in beer, rich in leucoanthocyanins, are composed of peptones, peptides, and condensation products of the tannins of malts and hops.

Mashing begins with the mixing of crushed malt and water together with the boiled adjunct if used; this is called mashing-in. The mash is heated gradually to 78°C. During heating the mash passes through the optimum temperatures of the various enzymes. By holding the mash a certain time at various temperatures the composition of the wort is adjusted. At 78°C only α-amylase is partly active (its optimum is 70°C) and the mash is kept at 78°C to ensure that all starch material is totally decomposed. This is called mashing-off.

A great many mashing methods are found in the brewing industry. Fundamentally three different methods can be distinguished: (*1*) decoction methods where part of the mash is transferred from the mash tun to the mash kettle where it is heated to boiling and then returned to the mash tun; (*2*) infusion methods where the whole mash is heated gradually from mashing-in to mashing-off and no boiling occurs; and (*3*) mixed methods which are

combinations of (*1*) and (*2*). The mashing-in must be done in a way that evenly disperses the malt particles so that no lumps are formed. It is important to have a definite proportion of malt and water in order to have the desired density of wort. The mashing method must always be adjusted according to the type of beer, the quality of malt, and adjunct.

Decoction Methods. There are three types of decoction methods including the three-mash, the two-mash, and the one-mash method. The three-mash method (Fig. 6) is the oldest and best known decoction method, originating in Bavaria. The method is relatively time-consuming and uneconomical. The mashing-in is at 35–37°C. The first cook-mash, a part of the whole mash, is drawn off and transferred to the mash kettle where it is heated slowly to boil, then boiled for a certain time and pumped back to the mash tun. Here the temperature is raised to 50–55°C for the proteinase holding time. The second mash is drawn likewise, heated to boil, boiled, and pumped back to the mash tun where the temperature rises to 62–65°C, at the amylase holding time or saccharification temperature. The third mash undergoes the same treatment and the temperature in the mash tun ends up at 75–78°C. Total mashing time is about 5.5 h. The first one or two mashes are used for adjunct treatment and contain only small amounts of enzymes, but still enough to gelatinize the starch. The third mash is thin. This method may vary with the amount of cook-mashes. If a bigger volume is drawn off for the second cook-mash, the temperature in the mash tun after pumping back this second mash can be raised to 68–70°C which will result in a wort richer in unfermentable dextrins.

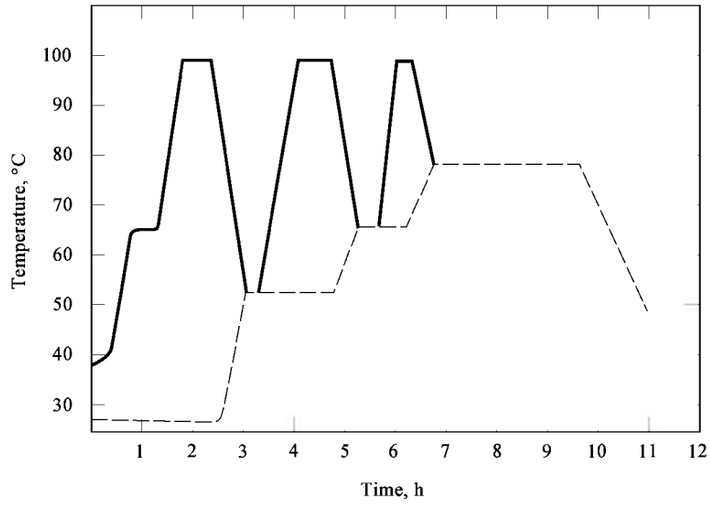

Fig. 6. Temperatures for a three-mash method. The solid line shows the temperature in the three-mashes that are boiled. The dashed line shows the temperature in the rest or whole mash, as the temperature is brought from mashing-on to mashing-off.

In a two-mash method, mashing-in is at ca 50°C. A first cook-mash brings the temperature to 60–65°C, and a second mash to 75–78°C. This method is used to obtain a wort of light color and good quality.

In a one-mash method mashing-in is usually at 60–65°C, holding this temperature for some time in the whole mash and then bringing the temperature to 75–78°C with the aid of one cook-mash.

Infusion Method. Infusion is a classic method for top-fermented beers and is used for all British types. The whole mash is heated gradually from mashing-in to mashing-off with holding times for the degradation of protein and starch. No part of the mash is boiled and the malt, therefore, must be well-modified to assure the breakdown of all soluble substances. Because no boiling takes place there is no physical breakdown of the malt, and consequently infusion is not as effective as decoction despite the better protection of the enzymes.

Mixed Methods. These are combinations of decoction and infusion methods. The mashing-in can be at 35–40°C, whereupon a cook-mash is drawn which, after having been boiled, brings the temperature to 60–65°C. After being held here for some time the whole mash is slowly heated, first to about 70°C then, after a short pause, to mashing-off at 75–78°C.

Separation of Mash. During mashing, all the valuable substances of malt and adjunct are broken down and dissolved. The mash contains sugars, nitrogenous substances, and husks. The undissolved part of the mash, called spent grains, is separated from the wort. Normally the strong wort is strained off first as completely as possible and the residual sugar is then sparged out using hot water of 75–78°C.

This separation process is time-consuming and consequently much effort has been spent to minimize the problem. Various practical ways have been invented, ie, the lauter tun, the mash filter, and the strainmaster.

The lauter tun is a cylindrical vessel provided with an extra perforated bottom about 1–10 cm above the real bottom. Using the lauter tun the wort is separated and sparged through a filter bed built up by the husks deposited on the perforated bottom. The yield is 3–10 brews per 24 h.

The mash filter is a plate and frame construction using filter cloth (cotton or polypropylene). The mash is pumped into the filter frames, the strong wort runs off simultaneously through the filter plates, and by the end of pumping the frames are completely filled up, ie, with husks only. The sparging is completed by pumping hot water 75–78°C from every second plate (eg, numbers 1, 3, 5, etc) through the neighbor frame to every second plate (eg, numbers 2, 4, 6, etc). The yield is 6–9 brews 24 h.

The strainmaster is a rectangular vessel construction fitted with a conical shaped bottom. The vessel is equipped with straining pipes horizontally orientated in the lower part. The advantage is that the pipes represent a larger filtration area compared to what is possible in a lauter tun; yields are up to 13 brews 24 h. The higher capacities in all three alternatives are gained, however, at the expense of higher extract losses and water consumption.

During the separation the strong wort and the sparge water run all together into the wort kettle for boiling, and the spent grains are sold as cattle fodder, or in some cases to bread manufacturers, and as such represent an important by-product of the brewing process.

Wort Boiling. The purpose of the boiling is to stabilize the wort microbiologically and enzymatically, to extract and isomerize the valuable substances of the hops to give the beer its characteristic taste and aroma (Table 10), and to evaporate a certain amount of water to give the wort its desired density (19). During the boiling the wort is sterilized effectively, all enzymes are destroyed so that their breakdown cannot continue during fermentation, and the so-called hot break sludge, colloidal protein, coagulates and precipitates. This process is aided by the action of tannins from malt and hops on proteins.

Table 10. Analysis of Worts[a]

Characteristics	Pale wort	Dark wort
extract, °P[b]	11.6	11.6
reducing sugars, maltose, °P[b]	8.3	6.8
reducing sugars, % of extract	71.5	58.6
final degree of apparent attenuation, %	79	68

total protein, % of extract	3.91	4.38
protein which is not precipitated by tannin, % of extract	3.62	4.02
amino acids, %	0.98	1.27
pH	5.62	5.47

[a] Ref. 20.

[b] °P °Plato, wt % extract (sugar).

The composition of carbohydrates and lower mol wt protein breakdown products in the wort are not affected by boiling. The latter are so degraded during mashing that they do not coagulate when boiled. In an acidic environment, at pH < 7, the higher mol wt proteins are precipitated by tannins, whereby two types of precipitations are formed. One type, the warm sludge or hot break, is stable and precipitated during boiling; the other type, the cold sludge or cold break, is reversible and precipitates during the cooling of the wort. The latter may contribute to the chill haze in beer.

Normally the wort is boiled vigorously for 1.5–2 h at atmospheric pressure. This vigorous boiling causes a strong turbulence whereby an even, intensive flow of bubbles rises from the heating area at the bottom of the kettle up through the wort. To attain a fine precipitation, the wort pH must be around the isoelectric point of the proteins, ca 5.0–5.2.

The extraction of the bitter substance of hops is a complex process. During boiling and subsequent fermentation, large losses of bitter substances are incurred, and only 25–30% of the bitter substances in hops are present in the finished beer. The amount of loss depends on composition of the wort, pH, etc. Much of these bitter substances is adsorbed by the warm sludge and is lost during its separation. Wort boiling takes place in the wort kettle or copper of various constructions. An example appears in Figure 7.

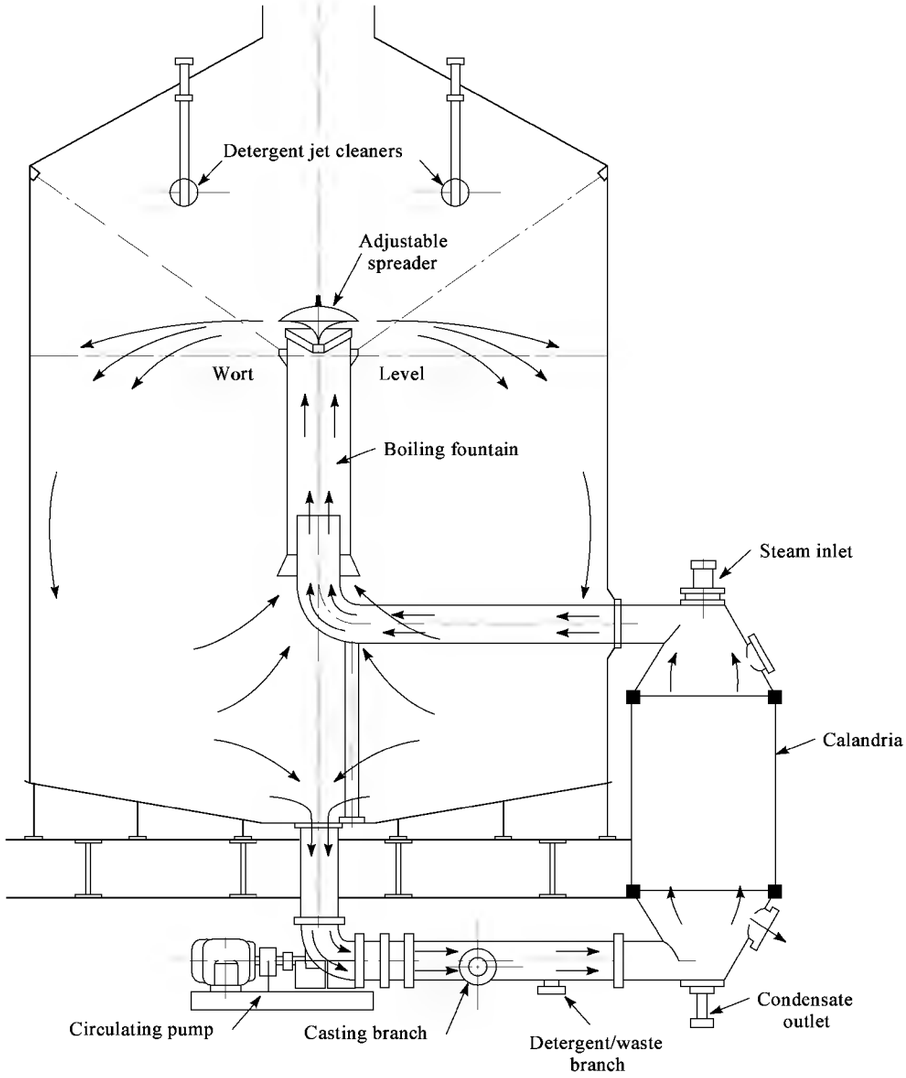

Fig. 7. Wort boiling kettle with external heating calandria. The wort is pumped from the bottom of the kettle through the calandria and thence back into the kettle through the so-called fountain. This circulation and heating may be started as soon as enough wort is in the kettle to fill the system. The directed flow from the spreader over the fountain reduces foaming.

Courtesy of Moosehead Breweries, New Brunswick, Canada.

During the last decade a lot of time and manpower have been spent in inventing new wort boiling systems, mainly to save energy and time. Evaporation rate is crucial. On one hand the lower the evaporation rate the better the result from an energy-saving point of view. On the other hand, a certain rate (8–10% h) is needed to get rid of the undesired volatiles, such as dimethyl sulfide, and obtain the density wanted. Tests have proven that the largest improvement is obtained by changing the evaporation rate from 7 to 4% per hour, and to a far lesser extent by the change from 11 to 7% per hour, which is the normal rate by traditional wort boiling at 100°C.

To save time, trials have been made by increasing the boiling temperature, such as low pressure boiling (LPB, 102–104°C) and high temperature boiling (HTB, 130–140°C). The time needed for boiling is thus reduced to 20 and 3 min, respectively, but unfortunately the evaporation rates in both cases are unsatisfactorily low. So far the results have not been fully successful because the quality of the beer is influenced too much. Low pressure boiling in combination with heat recovery from the steam might be a solution for the future, taking into account both energy-saving as well as the taste of the beer.

Treatment of the Wort. The hot wort produced in the brewhouse cannot be transferred directly to the fermenting room. If natural hops are used they must be separated by a hop strainer as shown in Figure 8. During boiling, protein–tannin complexes are precipitated in the form of warm sludge.

The warm sludge or hot break can be separated with various types of equipment, eg, a centrifuge, filter, or whirlpool. After this separation the wort is cooled in heat exchangers to the desired temperature for the addition of yeast. During cooling, at ca 50°C, the cold break begins to precipitate and many breweries choose to separate this as well. This cannot be done in a centrifuge because it does not have enough capacity and the cold break is too finely dispersed. The separation can be made by a kieselguhr filter. Before the wort reaches the fermenting room, oxygen must be added so that the yeast can propagate. This is done by injecting sterile air into the cooled wort. The amount of oxygen needed is about 8 mg L of wort.

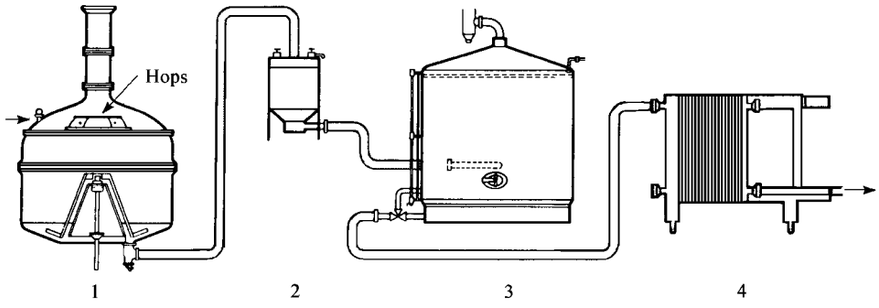

Fig. 8. Wort filtering in a whirlpool (1 = wort kettle; 2 = hop strainer; 3 = whirlpool tank; and, 4 = wort cooler).

The whirlpool was introduced in the early 1960s (Fig. 8). The tank is cylindrical with a flat bottom; its diameter in ratio to height is usually 1:1.4. The hot wort is led tangentially into the tank, approximately in the middle of its side.

As soon as the wort is cooled to <50°C it becomes an excellent culture medium for microorganisms. Therefore, the modern apparatus, in which the wort is cleared and cooled, is a closed system, completely isolated from the influence of microorganisms in the air, and is much safer in contrast to the old open coolships and open cooler.

Fermentation. During fermentation, sugars are converted into alcohol and carbon dioxide by the yeast (21). When the wort is cooled to the desired temperature, the yeast is added in the amount of 0.5–1.0% by vol of the wort or approximately 15 million cells per cm^3. The first indication of the fermentation appears within 12–24 h. When the wort is saturated with carbon dioxide, small bubbles appear on the surface and a creamlike froth is formed. The froth gets thicker and displays a series of highly regular formations from creamy low curls to foamlike high curls. Rising with the carbon dioxide are sediments which consist of hop resins and protein–tannin compounds. As the fermentation proceeds the foam subsides and drops, since fewer bubbles rise to support the cover. The increased alcohol content has an affect in this respect also. This is only visible for those who still use open fermentors. When the temperature has reached the preset highest degree, cooling is started for maintenance of constant temperature until the end of primary fermentation, in which most of the fermentable extract has been converted by the yeast.

Fermentation is carried out in two different, very distinct ways: top fermentation and bottom fermentation. The governing principles are the same in both processes; the chief differences are in the type of yeast and temperature employed, and consequently the method used for collecting the yeast after fermentation is finished. The alcohol content and, to a higher degree, the taste and stability of the beer, are directly dependent on the normal progress of the fermentation.

The yeast must be so finely dispersed throughout the wort that a quick yeast growth is assured, which leaves no possibility for other microorganisms, if any, to develop. The inoculation of yeast occurs through injection directly into the wort pipe. To be used in the next batch of wort, the yeast that is harvested after the end of fermentation must be protected against contamination.

Top fermentation is used in Great Britain for production of ale and stout. The yeast is usually a blend of pure strains of *S. cerevisiae*. Fermentation takes place in open vessels provided with equipment for harvesting the yeast from the surface. Figure 9 shows a time profile for a typical fermentation process in the traditional production of ale. After an initial phase, "the lag phase," the yeast begins to pick up nourishment from the wort for growth and fermentation, and the next phase involves a logarithmic growth of the yeast cells. Reproduction goes on until there is a lack of nourishment, ie, oxygen, amino acids, or minerals. Then fermentation continues until the fermentable substrate is exhausted. During reproduction, the temperature rises from 15 to 22°C. At this point, cooling is started to maintain a constant temperature. After 3–4 d the desired degree of fermentation is attained and the green beer is cooled from 22 to 14°C and is thus ready for secondary fermentation. Primary fermentation takes about six days and has four phases. In the first phase, a thin, white layer of foam is formed on the surface. In the second phase, this growth is thicker, higher, and darker because of hop resins. This layer is skimmed to prevent it from being mixed with the yeast that surfaces in the third phase. This yeast is pure, composed of fresh yeast cells, and it is also skimmed for later use for the brews to follow. In the last phase, the yeast turns to a hard, leathery layer; at this stage the beer is clearing.

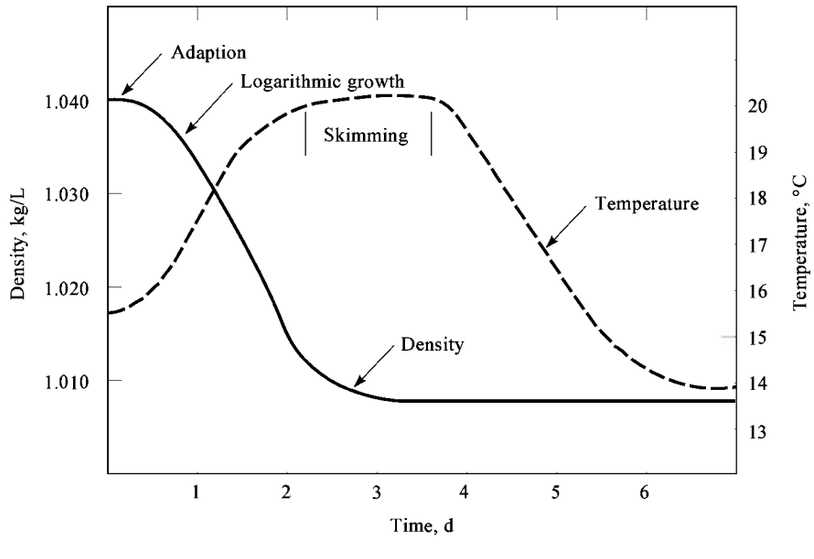

Fig. 9. Time profile for a typical fermentation with top yeast.

By tradition, top fermentation is carried out using methods that are named for the districts where they originated, eg, The Burton Union System and The Yorkshire Stone Square System. The first fermentation system is initiated in a hot temperated vessel for 36 h, then the fermenting wort is transferred

to a row of vessels. The fermentation continues and the developed carbon dioxide forces beer, foam, and yeast out through a hole in the upper part of the vessel and into a trough. Cooling is started and, by the end of fermentation, the yeast settles on the bottom of the trough. Yeast sedimented in the vessel is kept back when the beer is drawn off. This system, though it produces fine beer with a characteristic taste, is expensive.

Bottom fermentation is used for processing lager and other European beers. The yeast is *S. carlsbergensis* (uvarum). Figure 10 shows the relationship of density to time in a typical fermentation of lager beer. Fermentation takes place at considerably lower temperatures than top fermentation. Yeast is added at 6–10°C and the temperature is allowed to rise to 10–12°C before cooling sets in. Fermentation starts after 12–24 h. After 1–3 d the temperature reaches the prescribed highest point and fermentation is liveliest. By cooling, the temperature is kept constant for several days. In the last phase, the temperature is brought down to about 5°C. The fermentation gradually decreases. The yeast flocculates and precipitates and the beer is ready for lagering or maturation.

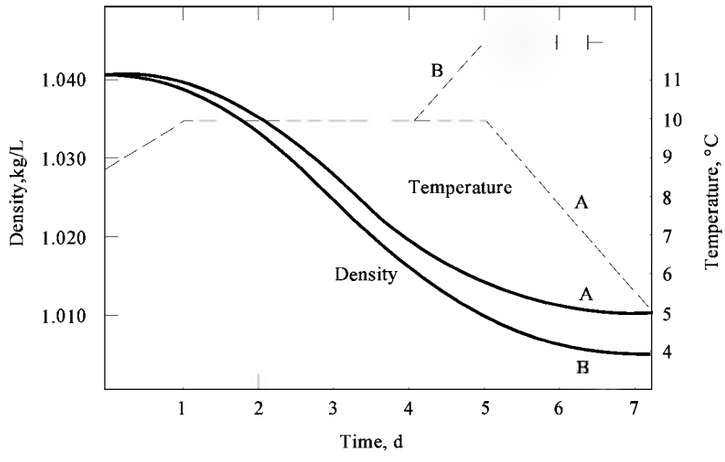

Fig. 10. Typical fermentation with bottom yeast. A, traditional fermentation; B, modern fermentation and forced maturation.

New Developments. Since the 1960s the fermentation of beer has undergone dramatic changes and developments, perhaps the most dramatic in the history of brewing so far.

In the early 1970s open fermentors and the continuous fermenting systems were found to be obsolete. The batch process was going to survive, and many new fermentor constructions appeared. The cylindroconical fermentor seemed to be the preferred solution for both a single- and a combi-vessel fermentation system, ie, fermentation and lagering in the same vessel (Fig. 11).

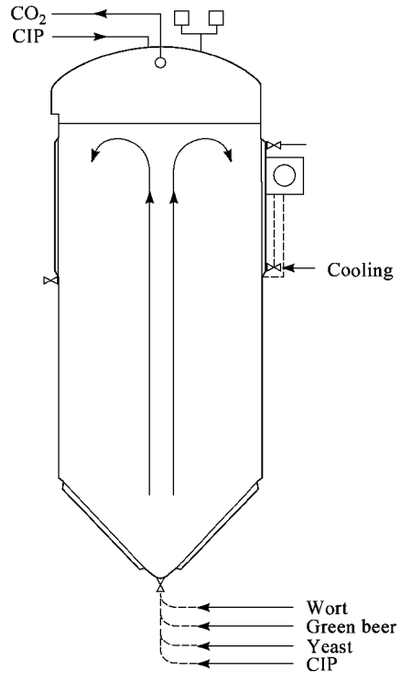

Fig. 11. Modern fermenting tank with conical bottom; CIP(cleaning-in-place) automatic cleaning system.

Today these vessels are built with a diameter:height ratio of 1 : <2 and the advantages are numerous. First, the temperature, as the most important parameter, is more correctly controlled, thus giving better probability of achieving the preferred temperature pattern. As an example the pattern might be as follows: the first 24 h an increase from 7–9°C to 10°C, 10°C is held for 3–4 d, then an increase from 10–12 15°C in the next 24 h, 12–15°C for a week, and finally cooling to 0–1°C over a period of 24–48 h, ie, a total of 13–14 d excluding one day for emptying and one day for cleaning (Fig. 10).

Consequently the total process time is reduced from at least five weeks to 16 d representing a reduction of 19 d or 54% . The resulting advantages are enormous compared to the traditional process.

The fermentation in these big vessels (max 3–5 brews) is normally performed pressureless, but several investigations have been made on fermentation under pressure and using somewhat higher temperatures in order to reduce the time needed still further. Some brewers agree with the statement that no yeast yet known can tolerate this extra stress and at the same time ferment a beer of equivalent excellent quality, but new selected yeast strains (genetic engineering) in the future may be better suited to these conditions.

Genetic manipulation or cloning offers many possibilities and perhaps there will be yeast strains especially designed for special beers, ie, types, which are useful because of low diacetyl formation, high–low ester formation, and insensitivity to pressure or high fermentation temperatures or extracellular enzymatic abilities (β-glucanases).

Beer Contaminants. Besides the culture yeasts, there are many wild yeasts, molds, and bacteria that may contaminate the beer. By constant cleaning, brewers try to keep to a minimum the number of harmful microorganisms. The infecting organisms are nonpathogenic because the low pH of the beer and antiseptic substances from the hops reduce the possibility of growth of pathogenic germs. The infecting organisms spoil the beer more or less according to the degree of infection in various ways, ie, increased acidity and off-flavors.

Foreign organisms capable of growing in beer are most often introduced through contamination of the inoculated yeast. Contamination from the air is of less importance, since open vessels are not commonly used any more. Thermo bacteria (gram-negative, lactic acid bacteria) are possible contaminants that cause spoilage of wort prior to fermentation. They have little effect on the flavor if they are subdued by quickly starting fermentation. Much more dangerous are the foreign organisms in pitching yeast because they grow in beer and compete with the yeast. Fortunately, the type of organism they may spread the most before being detected is wild yeast, which is not a great danger in modern breweries. Bacterial contaminations that produce acid and an off-flavor are dangerous because they multiply during all stages of fermentation, whereas yeast grows vigorously only during the initial phase. Lactic acid bacteria are among those that attack beer, both as rods such as different lactobacilli, and as cocci such as different pediococci, formerly called beer sarcina, that give off diacetyl *[431-03-8]*, $CH_3COCOCH_3$, and impart a butterlike flavor.

The presence of diacetyl at any stage of the process does not necessarily indicate an infection by pediococci, because diacetyl is normally formed during fermentation by oxidation of the precurser 2-acetolactate, which reaches a peak (1–1.2 ppm) at 24–36 h fermentation. The concentration of 2-acetolacetate is usually reduced to values of 0.01 ppm or less, and the diacetyl is reabsorbed by the yeast cells and enzymatically transformed through acetoin to butanediol. It is extremely important that 2-acetolactate as diacetyl is reduced below the threshold of 0.05–0.10 ppm (in terms of diacetyl).

During the lagering period, temperatures are generally so low that bacterial growth is insignificant. Bacteria carried through the filters have little chance to develop if the beer is pasteurized since this inactivates most microorganisms.

Lagering. The product of the primary fermentation process known as "green" beer is generally lacking in taste and stability. The taste is harsh and bitter, and has a peculiar yeasty aroma probably due to higher alcohols and aldehydes. Both the biological and the physico–chemical stabilities are unsatisfactory. This green beer must undergo a maturing process in which yeast and amorphous substances have sufficient time to settle to the bottom, the beer is saturated with carbon dioxide, taste and aroma are improved, and the chill-haze complex coagulates so that it can later be filtered off; at that point the beer must not have contact with air. Simple sedimentation does not make the beer satisfactory. To reach this goal the beer must be filtered.

Top-fermented beers are treated in various ways after the primary fermentation. The methods employed are called fining, ie, clearing of the beer with a colloidal gel, short conditioning without secondary fermentation, mixed fermentations, or conditioning in the bottle. Conditioning in bottles is used for many British export beers and special Belgian beers. The beer is clarified, either by filtration or by adding isinglass. It is then bottled, fresh yeast is added, and the bottles are kept horizontal at 15–20°C. The beer contains about 1% fermentable extract, which is fermented in about one week, whereby the beer is saturated with carbon dioxide. When the conditioning is finished, the bottles are raised and the yeast precipitates. The clear beer can then be decanted by treating the bottles carefully during pouring into the glass.

Bottom-fermented beer undergoes a secondary fermentation, or lagering, so that the beer will mature and become clear and saturated with carbon dioxide. The beer is pumped into lagering tanks and is kept for 1–4 months. This traditional maturing period has been reduced drastically under the new combi-process. At the beginning of lagering, the temperature is kept somewhat high to initiate the secondary fermentation, then lowered to 0–1°C, if possible. Normally this is adequate to obtain a satisfactory chemical stability; the beer is chillproof, but in some instances, ie, if something has gone wrong or if better stabilities are needed in export beers, an additional stabilizing process is necessary.

Several stabilization agents are available, ie, protolytic enzymes, tannic acid, or various adsorbents such as polyvinylpyrrolidinone (PvPP) and nylon-6,6 or bentonite. The stabilizing agent is normally added during the transfer to the stabilizing tank and left for some hours to react.

In modern stabilizing technology PvPP tends to be the preferred agent because it is most effective, insoluble, and imparts no trace of taste to the product. Unfortunately PvPP is expensive and consequently new techniques have been developed, ie, a secondary filtration using PvPP as filter aid including the possibility of regenerating the PvPP after stabilizing. By this regeneration only a few percentages of PvPP are lost each time, which is quite good compared with previous methods by which PvPP is lost totally after use.

Maturing improves the taste and aroma of beer and the elimination of tannin, protein, and hop resins also has a beneficial effect. Some metabolic products of unpleasant taste are further converted or washed out by the carbon dioxide surplus. The time for lagering varies with different types of beer. For every type of beer there is an optimal lagering time, and longer lagering is usually detrimental to beer quality. The filled lagering tanks are subjected to the saturating pressure of carbon dioxide, usually 50–70 kPa (ca 0.5–0.7 atm), controlled by a safety valve.

The temperature and extract content must be controlled regularly. Two weeks before bottling the beer should have a carbon dioxide content of 0.50 wt %, and samples are often taken for organoleptic tests.

Filtering. Conditioning or lagering gives the beer its desired organoleptic properties, but it still contains yeast, protein-tannin complexes, etc, ie, it has a hazy appearance. A high quality beer must be clear and totally sterile, have colloidal stability, and yeast must be removed to allow the beer to have biological stability. The protein-tannin complexes must also be removed so as not to upset the colloidal stability.

These substances are normally removed from the beer by filtration performed in different ways using different techniques, ie, pulp or mass, kieselguhr, sheet filtration, or a combination. Centrifuges might still be used when top-fermented beers are produced (Fig. 12). The mass filtration concept was commonly used all over the world in the 1940s, but has now been replaced by other methods in almost all modern breweries, because of serious disadvantages, ie, low capacities, no automation possibilities, high total costs, and inability to fulfill the high quality demands of today.

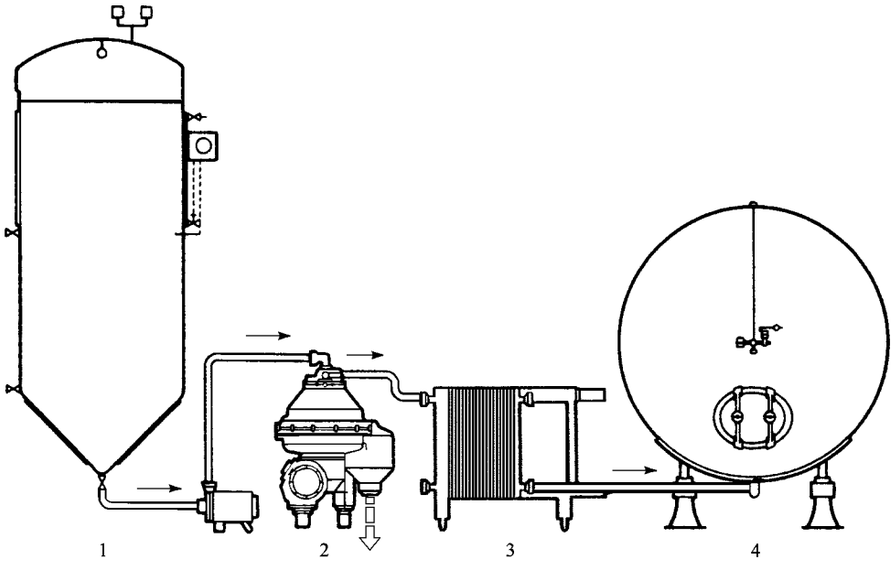

Fig. 12. Fermenting and storing (1 fermenting tank; 2 centrifuge (green beer separator); 3 green beer cooler; and, 4 storage tank).

Kieselguhr filtration, using different kinds of kieselguhr as filter aid (see DIATOMITE), is used in various filter constructions, ie, vertical leaf pressure filters, horizontal leaf pressure filters, candle filters, and plate and frame filters (Fig. 13 and Fig. 14). The filter constructions offered by four to five main producers vary in minor details, but in general the technique is the same. A coarse grade of kieselguhr is used as precoat, ie, it is distributed by recirculation, equally over the total filtration area. After precoating a mixture of beer, sludge, and an appropriate mixture of kieselguhr grades are pumped onto the filter and only the sparkling, brilliant beer runs through the filterbed to a pressure tank for control. In addition to required specifications, the most important consideration is that oxygen uptake during the entire filtration is as little as possible.

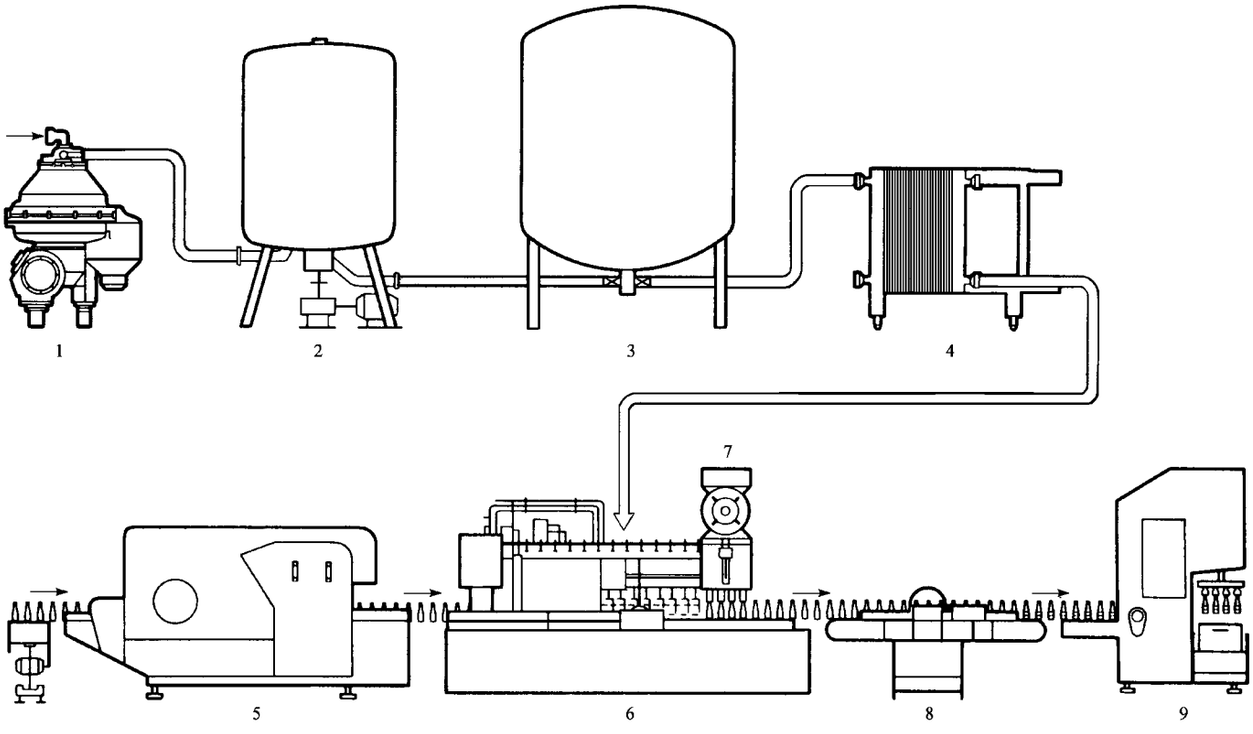

Fig. 13. Filtering and bottling (1 separator; 2 filter; 3 pressure tank; 4 = pasteurizer; 5 bottle washer; 6 filler; 7 crowner; 8 labeler; and, 9 = packer).

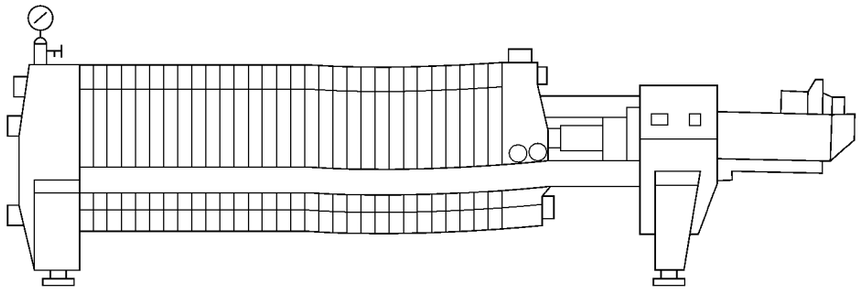

Fig. 14. Kieselguhr filter with plates and frames.

In some breweries it is of extreme importance that the beer be absolutely sterile, and therefore it is necessary to use a sheet filter filtration in addition to the primary filtration.

Few changes occurred during the 1980s as far as the filtration process and filter constructions are concerned. Automation is, of course, still a main topic and various new ways have been introduced to improve the working conditions (kieselguhr) and to reduce oxygen uptake during the whole process. New developments are necessary because kieselguhr sources might be depleted a few years after the year 2000, and consequently new filtration methods must be found. For this and for environmental reasons kieselguhr sludge is regenerated by burning and, to some extent, reused. The new membrane cross-flow technique is an interesting alternative, but many problems have yet to be solved before this method is practical.

Packaging. The beer in pressure tanks is transferred to bottling, canning, and racking, or in some cases, to road tankers. During this filling operation it is important that the beer does not come into contact with oxygen, does not lose carbon dioxide, and is not contaminated by molds, yeasts, or bacteria.

To prevent contact with oxygen, the beer in the pressure tanks is exposed only to a carbon dioxide atmosphere. The pressure must be higher than the saturation pressure for carbon dioxide. Infection in the brewery is prevented by daily cleaning and disinfection of all equipment in contact with the beer. In the past, almost all the beer left the brewery in kegs, but today most beer is bottled or canned. The ratio is different from country to country. The growing share of beer in bottles or cans has provided a great need for filling machines with capacities of up to 100,000 bottles or cans per hour.

Because of the demand for beer of extremely good stability, most beer today is pasteurized. During pasteurization most microorganisms are destroyed, and bacterial spores that do not grow in beer are left intact. Pasteurization guarantees nearly unlimited biological stability. Most beers are pasteurized in bottles or cans. The filled containers are transported through a pasteurizer. During passage, the beer is heated to pasteurizing temperature, kept constant for a set time, and then cooled to the desired temperature. In a modern pasteurizer each of these operations takes 20 min so that the total time in the pasteurizer is about one hour. This type of pasteurizer takes up much space and is expensive because of its high consumption of water, power, and heat.

Pasteurization does not mean sterilization of the beer, ie, killing all microorganisms, but rather a reduction and inactivation of the microorganisms. The result of the heat treatment depends not only on time and temperature, but also on the number of microorganisms present. It is important that tanks,

pipes, and filling equipment be scrupulously cleaned and protected against microbial contamination.

However, the relatively long heat treatment (30–40 min) of the traditional pasteurization of bottles and cans does have disadvantages. The most important is degradation of the quality of the taste. This is unavoidable, but the degree of degradation is proportional to the oxygen present in the beer and in the bottle neck (head space). If a low oxygen content is maintained in the bottles and cans, the extent of degradation is low and acceptable to some breweries. However, to provide an absolutely fresh, top-quality product, breweries use either flash-pasteurization or unpasteurized sterile filtered beer and aseptic bottling.

Two types of glass beer bottles today are the returnable bottle and the one-way or lightweight bottle. The one-way bottles are used in many countries but they are chiefly used for export because of their light weight and smaller size. In many countries return bottles are preferred because they are cheaper in the long run and better for the environment.

The first beer can was a conical top can with a wax coating on the inside; it was used before the present lacquer systems had been developed. The flat-top can was an outgrowth of the conventional food can, but it needed new conveying, filling, and seaming techniques. The aluminum ring pull-tab in 1964 started a revolution for beer canning. Jet-soldered cans reduced the width of the seam and permitted full wraparound graphics. Of equal and utmost importance to the canning breweries was the introduction of the drawn aluminum can. By the 1990s this had become the predominant can, which covers a large percentage of the total one-way market.

In recent years a tense discussion concerning the pros and cons of one-way versus returnable packaging materials in general has taken place. The reason is the debate on environmental protection and energy-saving theories, and supporters of the two systems are, of course, strong opponents. In the EC-countries, in the future the previous liberal conditions will likely be substituted by more restrictive policies dealing with packaging sizes and materials. This situation has already been witnessed by blacklisting the use of PVC packages by some retail companies.

Poly(ethylene terephthalate) (PET) bottles have been used for some time as an alternative to glass and aluminum. At first one-way bottles in different sizes were used; returnable PET-bottles of reasonable quality have been marketed. In the future, returnable PET-bottles will be used. The first examples of total production lines have been exhibited, ie, blow-form-fill-seal in an extra superblock construction.

The trend in general is somewhat contradictory, ie, the single package is growing bigger and bigger (up to 5 L) and consumers do not want to carry more than necessary at a time from the big and more centrally situated retailers.

Since a large part of the beer market is take-home beer, brewers must provide retailers with packs that are easily handled and stored. Clear shrink wrapping has become a dominant feature because it permits the content of the pack to be seen. Other packaging methods are Shrink Wrapped 2 dozen Tray Pack, Cardboard Sleeve, Hi Cone 3 Pack, Hi Cone 6 Pack in Tray, and Top Clip Bottle Pack (see PACKAGING MATERIALS).

New Developments. Changing the basic methods of production worries brewers because these changes may cause a deterioration in the quality of their product. Much has changed in the technology of beer making; however, the methods of transforming barley into beer have not undergone profound modifications because of the lack of fundamental knowledge. This lack is common to the whole food industry for several reasons. Food industries deal with transformations of living materials and their complex reactions. Raw materials are extremely variable. Barley and hops have numerous varieties with different hereditary characteristics. Their composition also differs according to the soil in which they are grown and the time of year when they are harvested. Yeast is subject to mutations. The reactions during the various stages of production are of an enzymatic and colloidal nature; therefore, the quality of the product is difficult to define. Health and safety legislation gives little room for use of new barley, enzymes, stabilizers, sugar substitutes, etc, but the situation can be different from one country to another.

In the brewing industry, caution is always used in changing anything for fear that it will adversely affect the product. However, brewers who maintain research and development staffs and have studied all phases of beer production well in advance of planned changes, feel they do have the information to design intelligently and adopt new equipment, new processes and procedures, and to employ an assortment of brewing ingredients usefully.

The degree of automation varies widely and generally most automation systems are based on computer techniques. Newer plants have the ultimate in automatic wort production where one person per shift, per brewhouse unit, makes up to 12 brews per day. An important consideration in current brewhouse operations is the increase in utilization of all vessels by the rapid batch process. A rapid filtration of grains is required and achieved with the use of a lauter tun, mash filter, or strainmaster. Of course the brewer sacrifices yield of brewhouse extract to achieve this high plant capacity, ie, the higher brewing rate results in an increase in plant capacity return on capital investment and labor productivity, but also gains higher extract losses.

The separation of hops from the boiled wort has been accelerated by the use of hop pellets or hop extract. The wort is transferred directly from the wort kettle to a whirlpool where the hops are separated along with the hot sludge. Whirlpools have become popular because of their low operating costs. In the whirlpool, hops and hot sludge break at the bottom, allowing the clarified wort to be drawn off.

High gravity brewing involves the production of worts with high initial gravity, and the introduction of a substantial portion of water at as late a stage in the conventional brewing process as possible, usually after primary or final filtration. This technique is popular because brewhouse, fermenting, and storage facilities do not have to be enlarged for increased production and it has no negative effect on the quality of the product if the additional water volume is less than about 20%. It can, however, result in a decrease in brewhouse yield, especially when corn or rice grits are used as adjunct. The volume of mash foundation water cannot be changed, thus the volume of sparge water must be radically reduced. Extract losses can be minimized by using corn syrup as the brewing adjunct which is added directly to the wort kettle during boiling.

A further development in the process is the use of universal refrigerant-cooled tanks, designed to ferment, age, and finish beer in a single tank without the usual transfers. The Uni-Tank has a shallow cone bottom rather than the typical steep cone shape of usual fermenting tanks. Fermentation and maturation of the beer within a single vessel take approximately two to three weeks.

The production of concentrated beer is basically a crystallization process in which water, constituting about 90% of a normal beer, forms pure ice crystals at temperatures below the freezing point of water which are separated from the beer concentrate (22). In this manner beer can be reduced to as little as one quarter of its original volume. After filtering, the beer concentrate is ready for reconstitution by the addition of water and carbon dioxide. Nothing is added to the beer at any point in this process that would facilitate the concentration or the reconstitution of the beer. This may be thought of as a sort of lagering process. Traditionally, ruh beer (beer that is fully fermented during maturing) is held in large storage tanks for weeks after fermentation is completed in order to carry out proper lagering and maturing. During this period certain constituents are precipitated from the beer. In the concentration and subsequent filtering step some of the constituents that contribute to the instability of finished beer are removed. Since these processes can be accomplished in a matter of hours, the resulting beer can be ready for consumption shortly after fermentation is completed, rather than weeks later as is the case with present lagering techniques. The motivation for this production of concentrated beer was originally to save transportation costs for export oriented breweries. But since this export has been substituted by licensed productions the importance of this technique has diminished.

In recent years, the automatic regulation of processes has steadily gained a foothold in the brewing industry. The aim has been to produce beer with a better and more even quality and at lower costs. Today, with new equipment and experience in automation within the process industry, it is possible to build an advanced automatic system for the brewing industry. Many factors influence the level of automation needed, and judgment must be used to decide what is best for optimum profit.

Since the 1970s an interesting evolution has been the concept of mini-breweries or pub breweries, which began in the United States, especially in towns of a reasonable size without "their own domestic brewery." The idea has spread to Europe and Asia, and the result is several thousands of small breweries, serviced by one or two persons, all over the world.

In the large tied houses or big independent pubs the installation of the so-called beer drive system, ie, beer supplied by tankers to relatively big cellar tanks combined with sophisticated beer dispensing systems, has been used successfully. The beer drive system might be seen as an alternative to the pub breweries or something which happened prior to the pub brewery period.

Alcohol Free Beer and Low Alcohol Beer. During Prohibition in the United States (1919–1933) efforts were made to produce beer that had low alcohol content. During World War II (1939–1945) efforts were again made for that purpose. Today, campaigns against driving while intoxicated have renewed this interest and many breweries are trying to produce beers with little or no alcohol, which also taste and smell like normal beer. The following methods have been suggested (23): interruption of fermentation, vacuum distillation, and reverse osmosis. Of these methods reverse osmosis is becoming more and more dominant, as far as reduced alcohol beers are concerned.

The beers in Table 11, with the exception of lunch beer, have an original gravity of 6.4–8.1°P. The alcohol content is 0.65–3.4% vol; the remaining extract is 3.9–7.1°P. Since the aroma of beers is obtained mainly during fermentation, beers having little or no alcohol produced with no or interrupted fermentation are lacking in "true" beer aroma. Previously aroma was improved through addition of small amounts of yeast (2–10 mg/L) to the unfermented beer. The addition usually takes place just prior to filtration.

Table 11. Properties of Low Alcohol Beers[a]

	Belgian beer	Malti-beer	Anti-mille	Hьmmer	Alcohol reduced	Lunch beer
original gravity, °P[b]	6.4	8.1	7.7	6.9	7.3	11.3
alcohol, vol %	0.8	0.65	1.13	1.3	2.2	3.4
extract, real, °P[b]	5.2	7.1	5.9	4.9	3.9	6.3
degree of fermentation, %	23.2	15.2	28.9	36.4	58.0	55.0
pH	4.64	4.77	5.06	5.18		4.70
bitter substances, mg/L	12.2		25.6	36.4		
kJ/L[c]	1075	1370	1280	1140	1175	1850

[a] Ref. 23.

[b] °P = °Plato, wt % extract (sugar).

[c] To convert kJ to kcal, divide by 4.184.

Cleaning and Disinfection.

Cleaning and disinfection of brewery equipment at every stage of the process is of vital importance. Physical cleanliness requires removal of all visible contaminations from the treated surfaces. Chemical cleanliness is obtained when all invisible contaminations are removed. Bacteriological cleanliness is obtained through disinfection of the equipment. This degree of cleaning must be obtained even if physical and chemical cleanliness are not. In breweries both chemical and bacteriological degrees of cleaning are nearly always obtained.

Disinfection can be performed in different ways, eg, by heat or chemical treatment. In breweries it is usual to use either water, at 90°C, or chemical agents. A disinfecting medium should act quickly even at low temperatures. The agent, moreover, must not be poisonous to humans or affect taste, aroma, and stability of beer. Some microorganisms may be resistant to a disinfectant after prolonged use. This risk can be eliminated by using very highly concentrated solutions, but it may sometimes be necessary to change disinfection agents.

Cleaning-In-Place (CIP) means application of a cleaning solution through equipment and apparatus which does not have to be dismantled after cleaning. The solution is pumped over the surfaces to be cleaned and a mechanical treatment occurs, ie, by spraying with special nozzles and a pressure of about 400 kPa (4 atm) which gives the solution a velocity of at least 1.5 cm/s and good turbulence. Rinsing water, cleaning solutions, and disinfecting agent are kept in tanks in the CIP station. The equipment includes pumps, pipes for circulation, and valves and filters to remove large particles from the solutions. The CIP station includes a heat exchanger, if hot cleaning is preferred, and is often fully automated.

Service Processes of the Brewery

The brewing process consumes great amounts of energy in the form of electricity and heat. Heat is used either as steam or heated oil. High temperature oil systems are popular in newer constructions because they are easier to regulate and maintain and the investments are lower. The total heat consumption varies considerably from one brewery to another depending on equipment, method of production, and size. As in other industries, precautions are taken to minimize energy consumption. A well managed brewery (>1 × 10^6 hL/y) uses 216–252 MJ/L (60–70 kwh/hL = 7750–9050 BTU/U.S. gallons) total energy for heating, cooling, and lighting. The heating component, ie, 180 MJ/L (50 kwh/hL), is used in the brewhouse (about 33%), for heating the premises (about 33%), and the remainder at other stages in the production. Normally the amount of hot water provided for in the brewhouse by wort cooling and steam condensation is more than required in the brewhouse, and the excess is used in other departments.

Electricity is often bought from the local distributors as high voltage current of 3–20 kV, which is transformed to normal working voltage of 380 V by the brewery's transformer. The consumption of electrical power is usually 36–72 MJ/L (10–20 kwh/hL = 1300–2600 BTU/U.S. gallons) of beer produced. Motor use accounts for 80–90%, and of this half goes to cooling.

Cooling is performed in a closed circuit where the cooling medium, ammonia, changes from liquid to gas. The gas phase is compressed from 100–200 kPa to 1–2 MPa (1–2 atm to 10–12 atm) and is cooled by water, and thus condensed and liquified. The pressure in the liquid phase is held at 100–200 kPa, corresponding to a temperature of −20 to −10°C. At a later stage, when cooling is required, the liquid is evaporated and sucked to the compression unit at a pressure corresponding to the temperature needed, ie, −2°C in fermentors. The whole cooling system is easily automated.

Compressed air is used for various purposes. Air which might come into contact with the product must be free of odor, particles, and oil, have a pressure dew point at less than 2°C, and be sterile. The air is normally compressed to 1000 kPa (8–10 atm) and cooled directly after the compressor. If needed, the air is then further dried by an absorbtion unit and the small particles and germs are removed through a set of filters of declining pore size.

Carbon dioxide is used to increase the natural CO_2 content of the beer and as counterpressure in tanks and filling machines. It must be free of water and any aroma. The consumption is 0–10 g/L of beer produced. In major breweries, carbon dioxide is bought in bulk, and in many breweries it is common practice to collect the surplus CO_2 from the fermentors to clean, dehumidify, and compress in a local CO_2 plant which is easily automated.

Economic Aspects

Beer enjoys a unique popularity all over the world. From 1975 to 1985 total world beer production rose from 798 × 10^6 hL to 1012 × 10^6 hL or an increase of 26.8%. However, in some of the traditional beer producing countries the production has decreased, and in other areas the increase is more than 26.8% (Table 12). One of the reasons for this is the fact that licensed production has become more popular.

Table 12. World Beer Production in 1988[a]

Country	Production, 10^3 hL	Country	Production, 10^3 hL
Americas		*Europe*	
United States	231,500	Federal Republic of Germany	92,639
Canada	23,837	United Kingdom	60,280
Mexico	34,131	USSR	54,000
Brazil	47,800	Spain	26,579
Colombia	18,000	German Democratic Republic	24,400
Venezuela	13,000	Czechoslovakia	22,670
Peru	6,700	France	19,959

Argentina	5,950	Netherlands	17,526
Cuba	3,320	Belgium	13,792
Chile	2,657	Poland	12,257
Bolivia	1,280	Italy	11,191
Ecuador	1,200	Yugoslavia	11,000
Dominican Republic	1,139	Hungary	9,480
Jamaica	1,100	Austria	9,015
Panama	980	Denmark	8,600
Guatamala	900	Ireland	5,401
Paraguay	800	Portugal	5,325
Costa Rica	746	Sweden	4,350
El Salvador	690	Switzerland	4,100
Honduras	680	Finland	3,645
Uruguay	640	Norway	2,080
Puerto Rico	526	Luxemburg	635
Trinidad	450	others	24,016
Nicaragua	300	*Total*	*442,940*
Guiana	164		
Barbados	110	*Others*	
Surinam	99	African countries, total	55,670
Martinique	66	Asia	149,200
Bahamas	61	Australia	24,500
Haiti	60	Turkey	2,650
others	371	Israel	4,250
Total	*399,257*	*World total*	*1,078,467*

[a] Ref. — Brauwalt 1990.

Great Britain. A variety of beers are produced in Great Britain. Although the predominant beers are ales of different color and original gravity, stout and lager have a significant proportion of the market, ie, the share of the total market in 1985 was 39% for lager. Draught beer still shares 78% of the market and there is no indication of a change in that respect.

The beer is taxed with a basic rate on the wort gravity of 1030° and an extra rate for each additional degree of gravity. For example, in 1985 about 50¢ L at 1030° and 1.5¢ L for each additional degree. The tax is based on wort production, but includes an allowance for a legitimate loss of 6%. Production has decreased from 64.6 × 10^6 hL in 1975 to 60.3 × 10^6 hL in 1988. Per capita annual consumption was 111 L in 1987.

Germany. Beer production in Germany is divided into a large variety of beers including bottom-fermented (80–85%) and top-fermented (15–20%); this ratio is fairly stable. The ratio draught:packaged beer is 29:71 and is also stable. German beer legislation is called "Reinheitsgebot" or "the Purity Law", which stipulates that beer must be made from barley malt, hops, yeast, and water only; it was applied to beers consumed in Germany, that had been brewed in Germany as well as imported, until 1988. Now, based on the verdict from the EEC Court in Luxembourg, imported beer produced by using some kind of adjunct is allowed on the German market, if the beer is legal in the producing countries.

The taxation system is progressive depending on both the volume produced and the original gravity, and the tax is levied on a shipments basis when the beer leaves the brewery.

The production of beer changed very little, from 93.4 × 10^6 hL in 1975, to 92.6 × 10^6 hL in 1988 (FRG only), but there were ups and downs in the period. Per capita consumption was 145 L in 1987.

France. In France, beer production is concentrated in the northern and eastern parts of the country. Beer production decreased from 22.3 × 10^6 hL in 1975 to 19.9 × 10^6 hL in 1988; packaged beer amounts to about 80% of the total. Per capita consumption was about 48 L in 1987.

The Netherlands. The proliferation of beer types in the Netherlands is less pronounced compared with the neighboring countries. The most popular beer (alc 5 vol %) accounts for 99% of the market. The ratio draught:packaged beer is 1:2 and fairly constant. The taxation point is the wort stage, before fermentation takes place, and tax is progressive on the basis of volume as well as of original gravity (volume degree ~hL°). Production increased from 12.2 × 10^6 hL in 1975 to 17.5 × 10^6 hL in 1988. Holland is still one of the greatest exporting countries of the world. Per capita consumption was 84.3 L in 1987.

Belgium. Belgium is ranked number four in Europe as far as per capita consumption is concerned (121 L in 1987), and consequently the brewing industry is an important factor in the economy of the country. The proliferation of beer types is very pronounced and may be the most interesting in Europe. The variety of beers available is enormous, due to monastery traditions which have played an important role in the evolution of the beer market. The old traditions have survived to a large extent, ie, the variation in gravity is large, top- and bottom-fermentated beers are marketed, fermentation in the bottle is still done, etc. The taxation is progressive and based both on volume as well as strength. Production has remained constant; it was 13.8 × 10^6 hL in 1975 and 13.8 × 10^6 hL in 1988.

Italy. Even though the consumption of beer nearly doubled during the 1980s, the brewing industry does not play an important role in the Italian economy. The per capita consumption of beer was 25.6 L in 1987. The proliferation of beer is low and beer below 10% in original gravity is not allowed. There are three types of beer with different original gravity, ie, 11°–13°P, 13°–15°P, and >15°P. The taxation is rather simple, ie, no progression, but a fixed tax on each hectoliter degree. Consumption increased from 6.5 × 10^6 hL in 1975 to 11.2 × 10^6 hL in 1988.

Denmark. In Denmark beer is a very popular beverage; the per capita consumption was around 125.2 L in 1987 and has remained stable. The types of beer are rather limited and in principle there are only six different categories. Top-fermented beers have more or less disappeared from the market and 85–90% of the consumption is the lager pilsner type of max 11.0°P. One brewery group accounts for 85% of the market. The taxation is relatively complicated, ie, every category is taxed separately on the packaged volume. The tax rate is one of the highest in the world and a VAT of 22% is added. Consumption decreased from 8.9 × 10^6 hL in 1975 to 8.6 × 10^6 hL in 1988. Only returnable packages are allowed.

Norway. Norway is ranked among the lowest alcohol consuming countries of the world; the per capita annual consumption was 51.4 L in 1987. There are very strict regulations in sales, advertizing, tax, etc. The four beer categories are taxed separately at a slightly progressive rate. Consumption increased only slightly from 1.9 × 10^6 hL in 1975 to 2.1 × 10^6 hL in 1988.

Sweden. In Sweden strict regulations of beverage consumption are more or less similar to those in Norway. Retail sales of normal beers (alc 4.3 vol %) and spirits are possible through government controlled stores (Systembolaget AB) only. The per capita consumption of beer was 51.4 L in 1987. The tax is paid on the basis of the packaged product when leaving the brewery and the rates are strongly progressive. The consumption of beers decreased from 4.9 × 10^6 hL in 1975 to 4.35 × 10^6 in 1988.

Finland. Here, too, restrictions are severe. Finland had total prohibition from 1919 until 1939, which destroyed the brewing industry. After repeal, new beer production was interrupted by World War II. The per capita consumption was 51.5 L in 1987. Production increased from 2.5 × 10^6 hL in 1975 to 3.6 × 10^6 hL in 1988.

Canada. The two predominant beer types are lager and ale. The preference for ale has decreased considerably over the years, from 60% in 1960 to 34% in 1984. The amounts produced of the porters and stouts have decreased also, from 1% to 0.02%. The approach to control the consumption of beer and other beverages is somewhat different in the provinces, especially as far as the retail sales are concerned (24). The per capita consumption was 82 L in 1987 and output increased from 20.8 × 10^6 hL in 1975 to 23.8 × 10^6 hL in 1988.

The United States. Although there are American breweries more than 100 years old, the brewing industry in the United States is young. With their technical and scientific expertise, American brewers are among the leaders in the brewing industry.

The United States' definition of beer is as follows. Beer shall mean beer, ale, porter, stout, and other similar fermented beverages of any name of

description containing >0.5% by volume of alcohol, brewed or produced from malt, wholly or in part, or from any substitute thereof. A cereal beverage shall mean a malt beverage, either fermented or unfermented that contains, when ready for consumption, <0.5% by volume of alcohol. These latter beverages are wholly tax-free, but the former must pay federal and state taxes without regard to beer strength, but related to the size of the brewery as far as the federal tax is concerned, ie, the tax is $0.23 per U.S. gallon ($0.06 L) up to a yearly output of 60,000 barrels (2.52×10^6 gallons 9.5×10^6 L) but $0.29 ($0.076 L) per U.S. gallon over 60,000 barrels.

Beers produced in the United States are nearly all of continental European types, although there are some ales of British style produced as well. The largest market is for the pilsner type with an original gravity of 11–12°P. They are light in taste, pale in color, rather bland, and with no pronounced hop aroma. In total production the United States brewing industry is the world's largest having an output of over 230×10^6 hL in 1988. The per capita consumption of about 90 L ranks below many other countries. The United States also have the world's largest breweries and five of them accounted for 95% of the beer market in 1988. Packaged beer accounted for 82% of beer sold in 1985.

Environmental Problems

Breweries must consider pollution of their effluent and also the availability of good quality incoming water; the price is going up rapidly. In the 1970s the beer:water ratio used was 1:10 or more, but today, in well managed breweries, it is 1:5–6, which is nearly impossible to improve further. The BOD level of effluent from breweries varies between 1000–2000 mg L. Normal household sewage water has a BOD level of 600 mg L; average BOD level exceeding 600 mg L is charged extra. Thus every company has an economic interest in producing effluents at as low a BOD level as possible. Table 13 shows the composition of the effluent in various steps of the brewing process, and likewise the most critical points. To minimize the polluting substances in the effluent, and consequently the payment, several things can be done. Traditionally the by-products of the brewery, ie, spent grains, surplus yeast, and carbon dioxide, have been separated and used reasonably for other purposes, but this could be done with more care. By careful handling of all relevant methods, ie, beer transfers, cleaning, cleaning solutions, disinfectants, spent kieselguhr, and sludge, the BOD level can be reduced to below 1000 mg L, and if the total water consumption has been reduced to 6 L per liter beer produced, this is probably the lower limit by traditional methods. Brewery effluents have favorable C N and N P ratios, ie, 8–10 times better than needed. In some cases the payment for pollution is so high that it becomes reasonable to build a plant for prepurifying the brewery effluent, and this has been done in several breweries.

Table 13. Composition of Effluents[a]

Process	Effluent content	BOD level
mashing	cellulose, sugars, amino acids, cleaning compounds	low
mash filtering	spent grains, sugars, amino acids, cleaning compounds	high
wort boiling	hops, wort, cleaning compounds	low
hop strainer	spent hops, wort, cleaning compounds	high
whirlpool	sludge, wort, cleaning compounds	high
fermentation	yeast, sludge, beer, cleaning compounds	high
lagering	yeast, protein, beer, cleaning compounds	high
beer filtering	kieselguhr, yeast, protein, beer, cleaning compounds	high
filling	beer, glass, crowns, cleaning compounds	high
bottle washing	beer, glass, labels, glue, oil, cleaning compounds	high

[a] Ref. 25.

In addition to considering the external environment, recommendations for the internal environment have been set. Every room in which human activity is required has maximum limits for noise (85–90 dB), carbon dioxide, solvents, radiation, temperature, etc.

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BENTONITE.

See CLAYS.

BENZAL CHLORIDE.

See CHLOROCARBONS AND CHLOROHYDROCARBONS.

BENZALDEHYDE

Benzaldehyde *[100-52-7]*, C_6H_5CHO, is the simplest and quite possibly the most industrially useful member of the family of aromatic aldehydes.

Benzaldehyde exists in nature, primarily in combined forms such as a glycoside in almond, apricot, cherry, and peach seeds. The characteristic benzaldehyde odor of oil of bitter almond occurs because of trace amounts of free benzaldehyde formed by hydrolysis of the glycoside amygdalin. Amygdalin was first isolated in 1830 from the seeds of the bitter almond (*Prunus amygdalus*). Sometime later Liebig and Wöhler found that when amygdalin was hydrolyzed with water and emulsin, benzaldehyde, hydrogen cyanide, and D-glucose were formed (1).

Physical Properties

Physical properties of benzaldehyde are listed in Tables 1 and 2; boiling points and concentrations of certain selected binary azeotropes are given in Table 3. For a more complete listing of benzaldehyde azeotropes see reference 3.

Table 1. Physical Properties of Benzaldehyde

Property	Value
molecular formula	C_7H_6O
molecular weight	106.12
boiling point, °C at 101.3 kPa[a]	179
melting point, °C	26
flash point, closed cup, °C	63
autoignition temperature, °C	192
refractive index, n^{20}	1.5455
viscosity, mPa·s (cP) at 25°C	1.321
density, g/cm^3 at 25°C	1.046
specific heat (liquid) at 25°C, J/(g·K)[b]	1.615
latent heat of vaporization[c], J/g[b]	362
standard heat of combustion, kJ/g[b]	31.9
solubility in water at 20°C, wt %	~0.6
solubility of water in at 20°C, wt %	~1.5

[a] To convert kPa to atm, divide by 101.3.

[b] To convert J to cal, divide by 4.184.

[c] At the boiling point (179°C).

Table 2. Vapor Pressure vs Temperature[a]

Temperature, °C	Pressure, kPa[b]
26.2°C	0.13
50.1°C	0.67
62.0°C	1.33
75.0°C	2.66
90.1°C	5.32
99.6°C	8.0
112.5°C	13.3
131.7°C	26.6
154.1°C	53.3
179.0°C	101.3

[a] Ref. 2.

[b] To convert kPa to mm Hg, multiply by 7.5.

Table 3. Binary Azeotropes of Benzaldehyde[a]

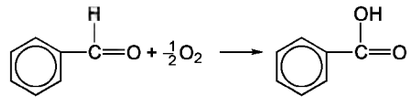
Component	Azeotrope, boiling point, °C	Benzaldehyde, %
benzyl chloride	177.9	50
o-cresol	192	23
D-limonene	171.2	43
cineole	172	36
phenol	185.6	49

[a] Ref. 3.

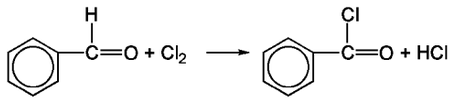
Chemical Properties

Benzaldehyde is a versatile intermediate because of its reactive aldehyde hydrogen, its carbonyl group, and the benzene ring.

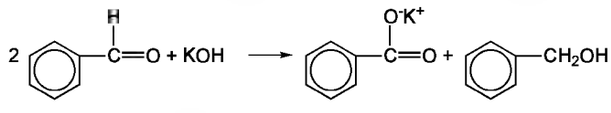
Aldehyde Hydrogen Reactions. The hydrogen of the aldehyde groupis readily oxidized to OH, forming benzoic acid *[65-85-0]*.



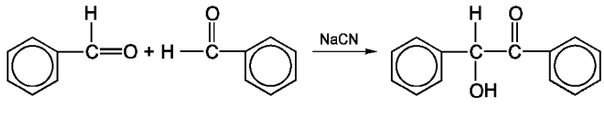
Chlorine can replace the hydrogen to produce benzoyl chloride.



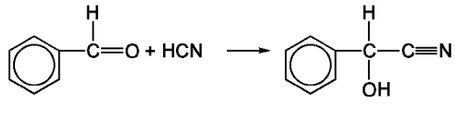
In the Cannizarro reaction, benzaldehyde is both oxidized and reduced to form benzoic acid (as the benzoate salt) and benzyl alcohol.



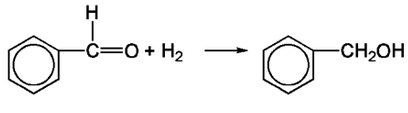
Alkali metal cyanides catalyze the condensation of benzaldehyde to form benzoin.



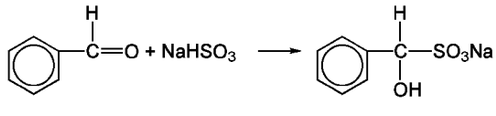
Carbonyl Group Reactions. Mandelonitrile *[532-28-5]* is formed by the addition of hydrogen cyanide to the carbonyl double bond.



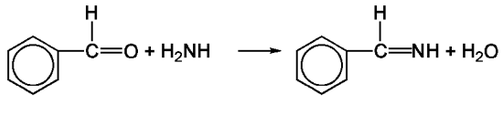
Hydrogenation of the carbonyl group yields benzyl alcohol.

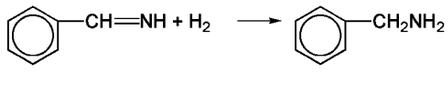


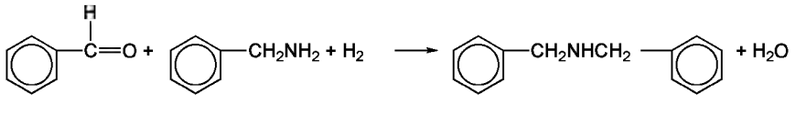
Sodium bisulfite adds to the carbonyl double bond to give a hydroxysulfonate (bisulfite addition compound).



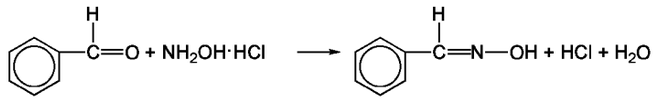
Schiff bases, also known as imines, are formed by the condensation of carbonyl compounds with ammonia or primary amines. Hydrogenation of the resulting Schiff bases forms amines, such as benzylamine and dibenzylamine.



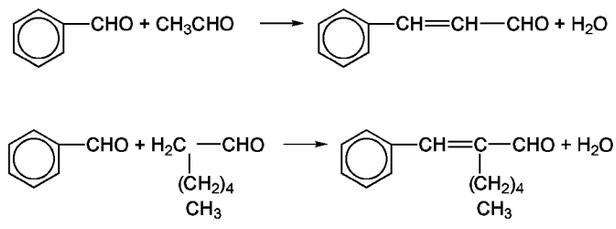




An assay method for benzaldehyde involves condensing benzaldehyde with hydroxyl amine hydrochloride to form an oxime. The released hydrochloric acid is then titrated.



Aldol additions of benzaldehyde with active methylene groups produce other aldehydes.



Benzene Nucleus Reactions. Ring substitutions, such as sulfonation and nitration, can be effected without destruction of the carbonyl group. Under the influence of the carbonyl group, meta substitution usually occurs.

Manufacture

The only industrially important processes for the manufacturing of synthetic benzaldehyde involve the hydrolysis of benzal chloride *[98-87-3]* and the air oxidation of toluene. The hydrolysis of benzal chloride, which is produced by the side-chain chlorination of toluene, is the older of the two processes. It is no longer utilized in the United States. Other processes, including the oxidation of benzyl alcohol, the reduction of benzoyl chloride, and the reaction of carbon monoxide and benzene, have been utilized in the past, but they no longer have any industrial application.

In the past benzal and benzyl chlorides were co-produced for the manufacture of benzaldehyde and benzyl alcohol, but today the vast majority of the benzaldehyde produced from benzal chloride is that which is made from recovered (by-product) material. For an historical article regarding the chlorination of toluene and the subsequent production of benzaldehyde, benzyl alcohol, and benzoic acid, see reference 4.

Today, the air oxidation of toluene is the source of most of the world's synthetic benzaldehyde. Both vapor- and liquid-phase air oxidation processes have been used. In the vapor-phase process, a mixture of air and toluene vapor is passed over a catalyst consisting of the oxides of uranium, molybdenum, or related metals. High temperatures and short contact times are essential to maximize yields. Small amounts of copper oxide may be added to the catalyst mixture to reduce formation of by-product maleic anhydride.

Conversion per pass is reported to be low, 10–20%, with equally low yields, 30–50% (5). The vapor-phase oxidation of toluene was the dominant toluene oxidation process in the 1950s and early 1960s, but is no longer of industrial importance. The liquid-phase process now dominates.

In the liquid-phase process, both benzaldehyde and benzoic acid are recovered. This process was introduced and developed in the late 1950s by the Dow Chemical Company, as a part of their toluene-to-phenol process, and by Snia Viscosa for their toluene-to-caprolactam process. The benzaldehyde recovered from the liquid-phase air oxidation of toluene may be purified by either batch or continuous distillation. Liquid-phase air oxidation of toluene is covered more fully (see BENZOIC ACID).

Economic Aspects

Benzaldehyde is produced in the United States by Kalama Chemical Incorporated, Kalama, Washington and in Canada by Chatterton Petrochemical Corporation, Delta, British Columbia. Both plants were constructed by The Dow Chemical Company in the early 1960s to produce phenol from benzoic acid and both produce benzaldehyde as a by-product of that process (6). Production and sales figures for benzaldehyde are not available.

Specifications and Test Methods

Benzaldehyde is sold as technical grade or as meeting the specifications of the *National Formulary* (NF) (7), the *Food Chemicals Codex* (FCC) (8), or the *British Pharmacopeia* (BP) (9) (Tables 4 and 5). The test methods used for the analysis of benzaldehyde are standard methods, with the exception of the assay method.

Table 4. *National Formulary* and *Food Chemicals Codex* Specifications

Specification	NF grade	FCC grade
assay[a], %	98.0–100.5	98.0, min
specific gravity at 25°C	1.041–1.046	1.041–1.046
refractive index at 20°C	1.544–1.546	1.544–1.547
chlorinated compounds	passes NF test	passes FCC test
hydrocyanic acid	passes NF test	passes FCC test
nitrobenzene	passes NF test	
solubility in bisulfite		passes FCC test

[a] Oximation method.

Table 5. *British Pharmacopeia* and Technical Grade Specifications

Specification	BP grade	Technical grade
assay,[a] %	98.0–100.5	98.0, min
density at 20°C, g/mL	1.043–1.049	
refractive index at 20°C	1.544–1.546	
chlorinated compounds,[b] % (w/v), max	0.05	none
free acid,[c] % (w/v), max	1.0	
color		colorless to pale yellow

[a] Oximation method.
[b] As chloride.
[c] As benzoic acid.

The assay method involves the reaction of benzaldehyde with hydroxylamine hydrochloride in an alcoholic solution. Benzaldehyde oxime, water, and hydrochloric acid are the products of the reaction. The hydrochloric acid formed is then titrated with standard caustic solution to determine the benzaldehyde assay.

Performing the titration to a potentiometric end point, rather than to a colored end point, has been shown to be the more accurate method. Since other carbonyl containing compounds also react to form the oxime and release hydrochloric acid, this test is not specific for benzaldehyde.

The levels of trace impurities in the product benzaldehyde are often more important than the product assay. Gas chromatographic methods for the determination of those trace impurities are widely used.

Health Effects

The oral LD_{50} for benzaldehyde is reported as 1300 mg kg in rats and as 1000 mg kg in guinea pigs. Based upon these values, benzaldehyde is considered a moderately toxic substance when ingested. The subcutaneous lethal dose in rats is about 5 g kg. The fatal oral dose in humans is estimated to be about 56.7 g (2 oz) (10). Benzaldehyde tested negative for mutagenicity in salmonella assays in the 1988 National Toxicology Program. Studies of the carcinogenic effects of benzaldehyde are currently in progress (11). In the industrial setting, exposure to benzaldehyde through eye and skin contact and inhalation is far more prevalent than ingestion incidence. Overexposure to benzaldehyde vapors is irritating to the upper respiratory tract and produces central nervous system depression with possible respiratory failure. Epileptiform convulsions have been observed in rabbits (10). Contact may cause eye and skin irritation. Some individuals are more sensitive to skin contact than others. See reference 12 for more toxicological information.

Safety and Handling

The low autoignition temperature of benzaldehyde (192°C) presents safety problems since benzaldehyde can be ignited by exposure to low pressure steam piping, for example. Benzaldehyde may also spontaneously ignite when soaked into rags or clothing or adsorbed onto activated carbon (13).

Bulk storage of benzaldehyde should be made under a nitrogen blanket, since benzaldehyde is easily oxidized to benzoic acid upon exposure to air. All storage tank openings should be easily accessible for cleaning, since they will have a tendency to plug with benzoic acid. Benzaldehyde is stored in noninsulated type 304 stainless steel storage tanks. If storage in very cold climates is contemplated, consideration should be given to insulating and steam-tracing the tank. A baked, phenolic, resin-lined tank is also suitable. Copper or brass are to be avoided since they are readily attacked by benzaldehyde and benzoic acid. Because of the low surface tension of benzaldehyde, the use of screwed piping fittings should be avoided (14).

Uses

Benzaldehyde is a synthetic flavoring substance, sanctioned by the U.S. Food and Drug Administration (FDA) to be generally recognized as safe (GRAS) for foods (21 CFR 182.60). Both "pure almond extract" and "imitation almond extract" are offered for sale. Each contains 2.0–2.5 wt % benzaldehyde in an aqueous solution containing approximately one-third ethyl alcohol.

"Natural" benzaldehyde can be produced in a number of ways. The FDA regulations regarding natural products are found in 21 CFR 101.22. At the present time there is a controversy over what the term natural really means with regard to benzaldehyde. Whether a particular benzaldehyde product is natural or not becomes an issue only if the final product is said to contain natural flavors.

There are at least two routes currently being used to produce natural benzaldehyde. Principal flavor houses are reported to market a product which is derived from cassia oil. The chief constituent of cassia oil is cinnamic aldehyde which is hydrolyzed into its benzaldehyde and acetaldehyde constituents. This is a fermentative retroaldol reaction. Whether this hydrolysis allows the final benzaldehyde product to be considered natural is of great concern. The FDA has reportedly issued an opinion letter that benzaldehyde produced from cassia oil is not natural (15).

The other significant production method for natural benzaldehyde involves the steam distillation of bitter almond oil which has been derived from the kernels of fruit such as apricots, peaches, cherries, plums, or prunes. The benzaldehyde product obtained in this fashion is claimed to have a superior flavor profile. The use of peach and apricot pits to produce the more profitable product laetrile apparently affects the supply available to natural benzaldehyde producers.

The subject of natural benzaldehyde came to the forefront in 1984 when it was found that a natural benzaldehyde product, labeled "oil of benzaldehyde," was actually made synthetically by the air oxidation of toluene followed by careful fractionation to remove trace impurities. This finding was accomplished by the Center for Applied Isotopic Studies, University of Georgia, and involved measuring the amounts of ^{13}C and ^{14}C in that material.

Benzaldehyde is also recognized as safe for use as a bee repellant in the harvesting of honey (21 CFR 180.2), and is authorized for use in denatured alcohol (27 CFR 21.151).

Benzaldehyde's most important use is in organic synthesis, where it is the raw material for a large number of products. In this regard, a considerable amount of benzaldehyde is utilized to produce various aldehydes, such as cinnamic, methylcinnamic, amylcinnamic, and hexylcinnamic.

Derivatives

Benzoin, *[119-53-9]*, 2-hydroxy-2-phenylacetophenone, $C_6H_5CH(OH)COC_6H_5$ (mp, 133–137°C; bp, 343–344°C at 101.3 kPa), is formed by the self-condensation of benzaldehyde in the presence of potassium cyanide. It is used on a small scale as a polymerization catalyst in polyester resin manufacture.

Benzil, *[134-81-6]*, diphenyl-α,β-diketone, $C_6H_5COCOC_6H_5$ (mp, 95°C; bp, 346–348°C at 101.3 kPa), formed by oxidizing benzoin is used as an intermediate in chemical synthesis.

Benzyl alcohol, *[100-51-6]*, $C_6H_5CH_2OH$ (bp, 205.4°C at 101.3 kPa), produced by the hydrogenation of benzaldehyde is used in color photography; as a parenteral solution preservative; as a general solvent; and as an intermediate in the manufacture of various benzoate esters for the soap, perfume, and flavor industries (see BENZYL ALCOHOL AND β PHENETHYL ALCOHOL).

Benzoyl chloride, *[98-88-4]*, C_6H_5COCl (mp, 1°C; bp, 197.2°C at 101.3 kPa; d^{25}_{4}, 1.2070; n_D^{20}, 1.55369), is a colorless liquid that fumes upon exposure to the atmosphere. It has a sharp odor and, in vapor form, is a strong lachrimator. It is decomposed by water and alcohol, and is miscible with ether, benzene, carbon disulfide, and oils.

Benzylamine, *[100-46-9]*, $C_6H_5CH_2NH_2$ (bp, 184°C at 101.3 kPa) produced by reaction of ammonia with benzaldehyde and hydrogenation of the resulting Schiffs base, is used as the raw material for the production of biotin (Vitamin H), as an intermediate for certain photographic materials, and as an intermediate in the manufacture of certain pharmaceutical products.

Benzylideneacetone, *[122-57-6]*, $C_6H_5CH{=}CHCOCH_3$ (bp, 260–262°C at 101.3 kPa; mp, 35–39°C) is produced by condensing acetone and benzaldehyde. It is used as an electroplating additive.

Benzylacetone, *[2550-26-7]*, $C_6H_5CH_2CH_2COCH_3$ (bp, 233–234°C at 101.3 kPa) is produced by condensing acetone and benzaldehyde, followed by selective hydrogenation, and is used in soap perfumes.

Dibenzylamine, *[103-49-1]*, $C_6H_5CH_2NHCH_2C_6H_5$ (bp, 300°C at 101.3 kPa) is produced by reaction of benzyl amine with benzaldehyde and hydrogenation of the Schiffs base. It is used in rubber and tire compounding, as a corrosion inhibitor, and as an intermediate in the production of rubber compounds and pharmaceutical products.

Cinnamaldehyde, *[14371-10-9]*, $C_6H_5CH{=}CHCHO$ (bp, 253°C at 101.3 kPa), produced by the alkaline condensation of benzaldehyde and acetaldehyde is the main ingredient in cassia oil. It is used in soap perfumes and as an intermediate in the production of other flavor and fragrance compounds.

α-Methylcinnamaldehyde, *[101-39-3]*, $C_6H_5CH{=}C(CH_3)CHO$, is produced by the alkaline condensation of benzaldehyde and propionaldehyde. Its principal use is as the raw material for *p-tert*-butyl-α-methyl dihydrocinnamic aldehyde, *[80-54-6]*, a lily of the valley fragrance intermediate.

α-Amylcinnamaldehyde, *[122-40-7]*, $C_6H_5CH{=}C(C_5H_{11})CHO$ (bp, 140°C at 0.7 kPa), produced by the alkaline condensation of benzaldehyde and *n*-heptaldehyde, produces a jasminelike floralness and is used extensively as a perfume for soap products.

α-Hexylcinnamaldehyde, *[101-86-0]*, $C_6H_5CH{=}C(C_{13}H_{27})CHO$ (bp, 174–176°C at 2 kPa), produced by the alkaline condensation of benzaldehyde and *n*-octaldehyde, also produces a jasminelike floralness and is used extensively as a perfume for soap products.

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BENZANTHRONE.

See DYES, ANTHRAQUINONE.

BENZENE

Benzene *[71-43-2]*, C H , is a volatile, colorless, and flammable liquid aromatic hydrocarbon possessing a distinct, characteristic odor. Benzene is used as a chemical intermediate for the production of many important industrial compounds, such as styrene (polystyrene and synthetic rubber), phenol (phenolic resins), cyclohexane (nylon), aniline (dyes), alkylbenzenes (detergents), and chlorobenzenes. These intermediates, in turn, supply numerous sectors of the chemical industry producing pharmaceuticals, specialty chemicals, plastics, resins, dyes, and pesticides. In the past benzene has been used in the shoe and garment industry as a solvent for natural rubber. Benzene has also found limited application in medicine for the treatment of certain blood disorders, such as polycythemia and malignant lymphoma (1), and further in veterinary medicine as a disinfectant. Benzene, along with other light high octane aromatic hydrocarbons such as toluene and xylene, is used as a component of motor gasoline. Although this use has been largely reduced in the United States, benzene is still used extensively in many countries for the production of commercial gasoline. Benzene is no longer used in appreciable quantity as a solvent because of the health hazards associated with it.

Benzene was first isolated by Michael Faraday in 1825 from the liquid condensed by compressing oil gas. He proposed the name bicarburet of hydrogen for the new compound. In 1833, Eilhard Mitscherlich synthesized bicarburet of hydrogen by distilling benzoic acid, obtained from gum benzoin, with lime and suggested the name benzin for the compound. In 1845, A. W. Hoffman and C. Mansfield found benzene in light oil derived from coal tar. The first practical industrial process for recovery of benzene from coal tar was reported by Mansfield in 1849. Coal tar soon became the largest source of benzene. Soon afterward, benzene was discovered in coal gas and this initiated the recovery of coal gas light oil as a source of benzene.

Until the 1940s light oil obtained from the destructive distillation of coal was the principal source of benzene. Except for part of the World War II period, the quantity of benzene produced by the coal carbonization industry was sufficient to supply the demand even when a large portion of benzene was used for gasoline blending.

After 1950, benzene in motor fuel was largely replaced by tetraethyllead but the demand for benzene in the chemical industry persisted and soon exceeded the total production by the coal carbonization industry. To meet this growing demand, methods for producing benzene directly from petroleum sources were developed.

Since the 1950s, benzene production from petroleum feedstocks has been very successful and accounts for about 95% of all benzene obtained. Less than 5% of commercial benzene is derived from coke oven light oil.

Benzene is the simplest and most important member of the aromatic hydrocarbons and should not be confused with benzine, a low boiling petroleum fraction composed chiefly of aliphatic hydrocarbons. The term benzole, which denotes commercial products that are largely benzene, is not common in the United States, but is still used in Europe.

Physical Properties

The physical and thermodynamic properties of benzene are shown in Table 1 (2). Azeotrope data for benzene with selected compounds are shown in Table 2 (3). Benzene forms minimum-boiling azeotropes with many alcohols and hydrocarbons. Benzene also forms ternary azeotropes.

Table 1. Physical and Thermodynamic Properties of Benzene[a]

Property	Value
mol wt	78.115
freezing point, °C in air at 101.3 kPa[b]	5.530
boiling point, °C at 101.3 kPa	80.094
density, g cm^3	
20°C	0.8789
25°C	0.8736
vapor pressure, 25°C, kPa[c]	12.6
refractive index, n_D, 25°C	1.49792
surface tension, 25°C, mN m (dyn cm)	28.20
viscosity, absolute, 25°C in mPa·s(cP)	0.6010
critical temperature, °C	289.01
critical pressure, kPa[b]	4.898×10^3
critical volume, cm^3 mol	259.0
heat of formation	
g, kJ mol	82.93
L, kJ mol	49.08
heat of combustion, kJ mol[d,e]	3.2676×10^3
heat of fusion, kJ mol	9.866
heat of vaporization, 25°C, kJ mol	33.899
solubility in H_2O, 25°C, g 100 g H_2O	0.180

[a] Ref. 2.

Courtesy of the Thermodynamics Research Center, The Texas A&M University System.

[b] To convert kPa to atm, divide by 101.3.

[c] To convert kPa to mm Hg, multiply by 7.5.

[d] To convert kJ to kcal, divide by 4.184.

[e] At 298.15 K and constant pressure to CO_2 and H_2O.

Table 2. Azeotropes of Benzene[a]

Component	CAS Registry Number	Bp, °C	Azeotrope Bp, °C	Azeotrope Wt % benzene
cyclohexane	*[110-82-7]*	80.75	77.56	51.9
cyclohexene	*[110-83-8]*	82.1	78.9	64.7
methylcyclopentane	*[96-37-7]*	71.8	71.5	9.4
n-heptane	*[142-82-5]*	98.4	80.1	99.3
2,2-dimethylpentane	*[590-35-2]*	79.1	75.85	46.3
2,2,4-trimethylpentane	*[540-84-1]*	99.2	80.1	97.7
methanol	*[67-56-1]*	64.72	57.50	60.9
ethanol	*[64-17-5]*	78.3	68.24	67.6
2-propanol	*[67-63-0]*	82.45	71.92	66.7
2-butanol	*[78-92-2]*	99.5	78.5	84.6
tert-butyl alcohol	*[75-65-0]*	82.9	73.95	63.4
water	*[7732-18-5]*	100	69.25	91.17

[a] Ref. 3.

Structure. The representation of the benzene molecule has evolved from the Kekule ring formula (1) to the more electronically accurate (2), which indicates all carbon–carbon bonds are identical.

(1)

(2)

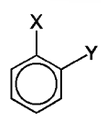
The bond angles and distances in benzene are known accurately from x-ray diffraction studies. The six carbon atoms form a regular hexagon in which each carbon atom is 0.139 nm from each of the two adjacent carbon atoms. The carbon–carbon bond lengths in benzene are intermediate in length between single and double carbon–carbon bonds. Each hydrogen atom is 0.108 nm from the carbon atom to which it is bonded. All twelve atoms lie in a single plane. All bond angles in benzene are exactly 120°.

Resonance Stabilization. Benzene has great thermal stability. It has a lower heat of formation from the elements than the corresponding structure (1) possessing three fixed, ethylene-type double bonds. Similarly, when benzene is decomposed into carbon and hydrogen, it absorbs more energy than is predicted by the Kekule formula. The hydrogenation of benzene is exothermic by about 208 kJ mol (49.8 kcal mol), about 151 kJ (36.0 kcal) less than three times the value for cyclohexene. This difference between the energy taken up during the formation of three double bonds and that obtained experimentally for benzene formation is termed the resonance energy for benzene (4,5).

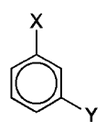
Chemical Properties

Benzene undergoes substitution, addition, and cleavage of the ring; substitution reactions are the most important for industrial applications.

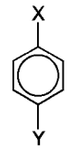
Electrophilic Aromatic Substitution. Benzene undergoes substitution of one or more of its hydrogen atoms by various groups such as halogen, nitro, sulfonic acid, or alkyl. Reactions with chlorine, bromine, or nitric acid are termed electrophilic aromatic substitution because they involve attack of electron-seeking reagents on the delocalized π-electrons of the aromatic ring. Similarly, benzene derivatives substituted with electronegative or electron-withdrawing groups undergo nucleophilic substitution reactions with electron-donating reagents. Benzene yields only one monosubstitution product and three possible disubstitution products, classified as ortho, meta, or para.



ortho



meta



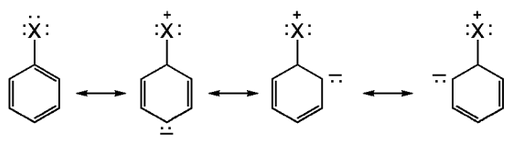
para

Table 3 shows the number of structural isomers possible when one, two, three, or four substituents, X, Y, and Z, replace the hydrogens of benzene.

Table 3. Number of Structural Isomers of the Substitution Products of Benzene

Substituents	Number of isomers
X	1
X, X	3
X, Y	3
X, X, X	3
X, X, Y	6
X, Y, Z	10
X, X, X, X	3
X, X, X, Y	6
X, X, Y, Y	11
X, X, Y, Z	16

Orientation in Electrophilic Aromatic Substitution. A substituent group that increases the rate of electrophilic substitution relative to benzene itself is called an activating group. Activating groups often have unshared electron pairs on atoms directly attached to the benzene ring and are characterized by their ability to contribute electron density to the π-orbitals of the aromatic ring, thus stabilizing the electrophile's influence on the ring (5,6). An example of a resonance effect is shown.



Resonance effects are the primary influence on orientation and reactivity in electrophilic substitution. The common activating groups in electrophilic aromatic substitution, in approximate order of decreasing effectiveness, are $-NR_2$, $-NHR$, $-NH_2$, $-OH$, $-OR$, $-NO$, $-NHCOR$, $-OCOR$, alkyls, $-F$, $-Cl$, $-Br$, $-I$, aryls, $-CH_2COOH$, and $-CH{=}CH-COOH$. Activating groups are ortho- and para-directing. Mixtures of ortho- and para-isomers are frequently produced; the exact proportions are usually a function of steric effects and reaction conditions.

Deactivating groups decrease the rate at which electrophilic aromatic substitution occurs. They lack an unshared electron pair on the atom directly connected to the aromatic ring and frequently are attached to an electronegative atom by double or triple bonds. The typical deactivating groups, in approximate order of decreasing effectiveness, are $-{}^{+}NR_3$, $-NO_2$, $-CN$, $-SO_3H$, $-CHO$, $-COOR$, $-COOH$, $-CONH_2$, and $-CCl_3$. Deactivating groups withdraw electron density from the π-electron cloud making the π-electrons less available for electrophilic reagents. It necessarily follows that, because of resonance effects, deactivating groups direct electrophilic substitution almost exclusively to the meta-position.

The entrance of a third or fourth substituent can be predicted by Beilstein's rule. If a substituent *Z*- enters into a compound C_6H_4XY, both X and Y exert an influence, but the group with the predominant influence directs *Z*- to the position it will occupy. Since all meta-directing groups are deactivating, it follows that ortho–para activating groups predominate when one of them is present on the benzene ring.

Nucleophilic Substitutions of Benzene Derivatives. Benzene itself does not normally react with nucleophiles such as halide ions, cyanide, hydroxide, or alkoxides (7). However, aromatic rings containing one or more electron-withdrawing groups, usually halogen, react with nucleophiles to give substitution products. An example of this type of reaction is the industrial conversion of chlorobenzene to phenol with sodium hydroxide at 400°C (8).

In nucleophilic aromatic substitutions, required reaction conditions become milder as the number of electron-withdrawing groups on the ring is increased. For example, the conversion of *p*-nitrochlorobenzene to *p*-nitrophenol occurs with sodium hydroxide solution at about 160°C. The conversion of 2,4-dinitrochlorobenzene to 2,4-dinitrophenol occurs with sodium carbonate solution at about 130°C. Picric acid (2,4,6-trinitrophenol) is obtained from the chloride by brief warming with water (9). The reaction occurs preferentially at ortho- and para-positions to electron-withdrawing substituents. In contrast to electrophilic aromatic substitution, electron-withdrawing groups such as NO_2 and CN are activating and ortho–para directing in nucleophilic aromatic substitution.

Nucleophilic aromatic substitutions involving loss of hydrogen are known. The reaction usually occurs with oxidation of the intermediate either intramolecularly or by an added oxidizing agent such as air or iodine. A noteworthy example is the formation of 6-methoxy-2-nitrobenzonitrile from reaction of 1,3-dinitrobenzene with a methanol solution of potassium cyanide. In this reaction it appears that the nitro compound itself functions as the oxidizing agent (10).

Oxidation. Benzene can be oxidized to a number of different products. Strong oxidizing agents such as permanganate or dichromate oxidize benzene to carbon dioxide and water under rigorous conditions. Benzene can be selectively oxidized in the vapor phase to maleic anhydride. The reaction occurs in the presence of air with a promoted vanadium pentoxide catalyst (11). Prior to 1986, this process provided most of the world's maleic anhydride *[108-31-6]*, $C_4H_2O_3$. Currently maleic anhydride is manufactured from the air oxidation of *n*-butane also employing a vanadium pentoxide catalyst. Benzoquinone *[106-51-4]*, $C_6H_4O_2$ (quinone) has been reported as a by-product of benzene oxidation at 410–430°C. Benzene can be oxidized to phenols with hydrogen peroxide and reducing agents such as Fe(II) and Ti(II). Frequently ferrous sulfate and hydrogen peroxide are used (Fenton's reagent), but yields are generally low (12) and the procedure is of limited utility. Benzene has also been oxidized in the vapor phase to phenol in low yield at 450–800°C in air without a catalyst (13).

Reduction. Benzene can be reduced to cyclohexane *[110-82-7]*, C_6H_{12}, or cycloolefins. At room temperature and ordinary pressure, benzene, either alone or in hydrocarbon solvents, is quantitatively reduced to cyclohexane with hydrogen and nickel or cobalt (14) catalysts. Catalytic vapor-phase hydrogenation of benzene is readily accomplished at about 200°C with nickel catalysts. Nickel or platinum catalysts are deactivated by the presence of sulfur-containing impurities in the benzene and these metals should only be used with thiophene-free benzene. Catalysts less active and less sensitive to sulfur, such as molybdenum oxide or sulfide, can be used when benzene is contaminated with sulfur-containing impurities. Benzene is reduced to 1,4-cyclohexadiene *[628-41-1]*, C_6H_8, with alkali metals in liquid ammonia solution in the presence of alcohols (15).

Halogenation. Depending on the conditions either substitution or addition products can be obtained by the halogenation of benzene.

Chlorine or bromine react with benzene in the presence of carriers, such as ferric halides, aluminum halides, or transition metal halides, to give substitution products such as chlorobenzene or bromobenzene *[108-86-1]*, C_6H_5Br; occasionally para-disubstitution products are formed. Chlorobenzene *[108-90-7]*, C_6H_5Cl, is produced commercially in the liquid phase by passing chlorine gas into benzene in the presence of molybdenum chloride at 30–50°C and atmospheric pressure. This continuous process yields a 14:1 ratio of chlorobenzene to *p*-dichlorobenzene *[106-46-7]*, $C_6H_4Cl_2$. The reaction of iodine with benzene takes place only in the presence of oxidizing agents such as nitric acid. Iodobenzene *[591-50-4]*, C_6H_5I, is thus produced from reaction of benzene, iodine, and excess nitric acid at 50°C (16). Benzene is fluorinated by direct liquid-phase reaction with fluorine in acetonitrile solution at 35°C. The reaction gives predominantly fluorobenzene with small amounts of *o*-, *m*-, and *p*-difluorobenzene by-products (17). Direct fluorination of benzene with fluorine has not yet gained commercial importance. Fluorobenzene *[462-06-6]*, C_6H_5F, is most commonly prepared from thermal decomposition of dry benzenediazonium tetrafluoroborate *[446-46-8]* (18).

Chlorine and bromine add to benzene in the absence of oxygen and presence of light to yield hexachloro- *[27154-44-5]* and hexabromocyclohexane *[30105-41-0]*, $C_6H_6Br_6$. Technical benzene hexachloride is produced by either batch or continuous methods at 15–25°C in glass reactors. Five stereoisomers are produced in the reaction and these are separated by fractional crystallization. The gamma isomer (BHC), which composes 12–14% of the reaction product, was formerly used as an insecticide. Benzene hexachloride *[608-73-1]*, $C_6H_6Cl_6$, is converted into hexachlorobenzene *[118-74-1]*, C_6Cl_6, upon reaction with ferric chloride in chlorobenzene solution.

Nitration. The nitration of benzene to nitrobenzene *[98-95-3]*, $C_6H_5NO_2$, occurs in yields often greater than 95% when a mixture of concentrated nitric and sulfuric acids is used at 50–55°C. Because the meta-directing nitro group is deactivating, the extent of nitration is rather easily controlled. To produce *m*-dinitrobenzene, more vigorous conditions are required, eg, nitric and sulfuric acids at 100°C. 1,3,5-Trinitrobenzene *[99-35-4]*, $C_6H_3N_3O_6$, is obtained from benzene with a large excess of fuming sulfuric and nitric acids at higher temperatures (19). When benzene reacts with mercuric nitrate and concentrated nitric acid, oxynitration occurs with the formation of either 2,4-dinitrophenol *[51-28-5]*, $C_6H_4N_2O_5$, or 2,4,6-trinitrophenol *[88-89-1]*, $C_6H_3N_3O_7$, depending on the reaction conditions (20).

Sulfonation. Benzene is converted into benzenesulfonic acid *[98-11-3]*, $C_6H_6SO_3$, upon reaction with fuming sulfuric acid (oleum) or chlorosulfonic acid. *m*-Benzenedisulfonic acid *[98-48-6]*, $C_6H_6S_2O_6$, is prepared by reaction of benzene-sulfonic acid with oleum for 8 h at 85°C. Often under these conditions, appreciable quantities of *p*-benzenedisulfonic acid *[31375-02-7]* are produced. 1,3,5-Benzenetrisulfonic acid *[617-99-2]*, $C_6H_6S_3O_9$, is produced by heating the disulfonic acid with oleum at 230°C (21).

Alkylation. Friedel-Crafts alkylation (qv) of benzene with ethylene or propylene to produce ethylbenzene *[100-41-4]*, C_8H_{10}, or isopropylbenzene *[98-82-8]*, C_9H_{12} (cumene) is readily accomplished in the liquid or vapor phase with various catalysts such as BF_3 (22), aluminum chloride, or supported polyphosphoric acid. The oldest method of alkylation employs the liquid-phase reaction of benzene with anhydrous aluminum chloride and ethylene (23). Ethylbenzene is produced commercially almost entirely for styrene manufacture. Cumene *[98-82-8]* is catalytically oxidized to cumene hydroperoxide, which is used to manufacture phenol and acetone. Benzene is also alkylated with C_{10}–C_{20} linear alkenes to produce linear alkyl aromatics. Sulfonation of these compounds produces linear alkane sulfonates (LAS) which are used as biodegradable detergents.

In recent years alkylations have been accomplished with acidic zeolite catalysts, most nobably ZSM-5. A ZSM-5 ethylbenzene process was commercialized jointly by Mobil Co. and Badger America in 1976 (24). The vapor-phase reaction occurs at temperatures above 370°C over a fixed bed of catalyst at 1.4–2.8 MPa (200–400 psi) with high ethylene space velocities. A typical molar ethylene to benzene ratio is about 1–1.2. The conversion to ethylbenzene is quantitative. The principal advantages of zeolite-based routes are easy recovery of products, elimination of corrosive or environmentally unacceptable by-products, high product yields and selectivities, and high process heat recovery (25,26).

ABB Lummus Crest Inc. and Unocal Corp. have licensed a benzene alkylation process using a proprietary zeolite catalyst. Unlike the Mobil-Badger process, the Unocal-Lummus process is suitable for either ethylbenzene or cumene manufacture (27,28).

Other Reactions. Benzene undergoes a number of other useful reactions.

Chloromethylation (Blanc-Quelet Reaction). Benzene reacts with formaldehyde and hydrochloric acid in the presence of zinc chloride to yield chloromethylbenzene *[100-44-7]*, C_7H_7Cl (benzyl chloride) (29), a chemical intermediate.

Friedel-Crafts Acylation. The Friedel-Crafts acylation procedure is the most important method for preparing aromatic ketones and their derivatives. Acetyl chloride (acetic anhydride) reacts with benzene in the presence of aluminum chloride or acid catalysts to produce acetophenone *[98-86-2]*, C_8H_8O (1-phenylethanone). Benzene can also be condensed with dicarboxylic acid anhydrides to yield benzoyl derivatives of carboxylic acids. These benzoyl derivatives are often used for constructing polycyclic molecules (Haworth reaction). For example, benzene reacts with succinic anhydride in the presence of aluminum chloride to produce β-benzoylpropionic acid *[2051-95-8]* which is converted into α-tetralone *[529-34-0]* (30).

Mercuration-Thallation. Mercuric acetate and thallium trifluoroacetate react with benzene to yield phenylmercuric acetate *[62-38-4]* or phenylthallic trifluoroacetate. The arylthallium compounds can be converted into phenols, nitriles, or aryl iodides (31).

Metalation. Benzene reacts with alkali metal derivatives such as methyl or ethyllithium in hydrocarbon solvents to produce phenyllithium *[591-51-5]*, C_6H_5Li, and methane or ethane. Chloro-, bromo-, or iodobenzene will react with magnesium metal in ethereal solvents to produce phenylmagnesium chloride *[100-59-4]*, C_6H_5MgCl, bromide, or iodide (Grignard reagents) (32).

Pyrolysis. Benzene undergoes thermal dehydrocondensation at high temperatures to produce small amounts of biphenyls and terphenyls (see BIPHENYL AND TERPHENYLS). Before the 1970s most commercial biphenyl was produced from benzene pyrolysis. In a typical procedure benzene vapors are passed through a reactor, usually at temperatures above 650°C. The decomposition of benzene into carbon and hydrogen is a competing reaction at temperatures of about 750°C. Biphenyls are also formed when benzene and ethylene are heated to 130–160°C in the presence of alkali metals on activated Al_2O_3 (33).

Manufacture

Benzene is a natural component of petroleum, but the amount of benzene present in most crude oils is small, often less than 1.0% by weight (34). Therefore the recovery of benzene from crude oil is uneconomical and was not attempted on a commercial scale until 1941. To add further complications, benzene cannot be separated from crude oil by simple distillation because of azeotrope formation with various other hydrocarbons. Recovery is more economical if the petroleum fraction is subjected to a thermal or catalytic process that increases the concentration of benzene.

After 1950, the demand for benzene exceeded the output by the coal carbonization industry and to supply the increasing demand, processes were developed for producing and separating benzene directly from petroleum feedstocks. The production of benzene from petroleum increased rapidly thereafter, and by the early 1960s the amount of benzene derived from petroleum was several times greater than that derived from coal. By the late 1970s coal-derived benzene accounted for less than 10% of total benzene produced. Although coke oven light oil often contains useful quantities of benzene, it is expected to further decrease as a source of aromatics as the number of steel companies that produce metallurgical coke from coal decreases.

Petroleum-derived benzene is commercially produced by reforming and separation, thermal or catalytic dealkylation of toluene, and disproportionation. Benzene is also obtained from pyrolysis gasoline formed in the steam cracking of olefins (35).

Catalytic Reforming. Worldwide, approximately 30% of commercial benzene is produced by catalytic reforming, a process in which aromatic molecules are produced from the dehydrogenation of cycloparaffins, dehydroisomerization of alkyl cyclopentanes, and the cyclization and subsequent dehydrogenation of paraffins (36). The feed to the catalytic reformer may be a straight-run, hydrocracked, or thermally cracked naphtha fraction in the C to 200°C range. If benzene is the main product desired, a narrow naphtha cut of 71–104°C is fed to the reformer. The reforming catalyst most frequently consists of platinum–rhenium on a high surface area alumina support. The reformer operating conditions and type of feedstock largely determine the amount of benzene that can be produced. The benzene product is most often recovered from the reformate by solvent extraction techniques.

Several significant reforming processes are in use (37,38). These include Powerforming (Exxon), Ultraforming (Standard Oil Co.), Rheniforming

(Chevron), Catalytic Reforming (Engelhard), and Platforming (UOP, Inc). Several other reforming processes are in use but these are limited to a few installations and are not of general interest (39). Platforming is a noteworthy example of current commercial reforming technology.

Platforming. The feedstock is usually a straight-run, thermally cracked, catalytically cracked, or hydrocracked C to 200°C naphtha (40,41) (Fig. 1). The feed is first hydrotreated to remove sulfur, nitrogen, or oxygen compounds that would foul the catalyst, and also to remove olefins present in cracked naphthas. The hydrotreated feed is then mixed with recycled hydrogen and preheated to 495–525°C at pressures of 0.8–5 MPa (116–725 psi) (42). Typical hydrogen charge ratios of 4000 to 8000 standard cubic feet per barrel (scf bbl) of feed are necessary (40). This is approximately equivalent to 700–1400 m^3 hydrogen per m^3 of feed.

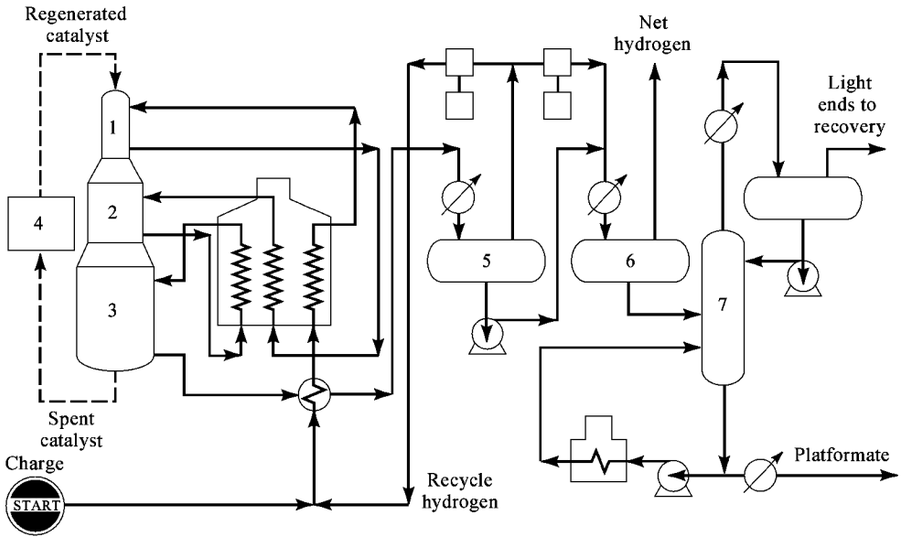


Fig. 1. Universal Oil Products Platforming process.

Courtesy Gulf Publishing Co., Houston, Tex. (41).

The feed is then passed through a stacked series of reactors. Usually three or four reactors are used (43,44). All of the reforming catalysts in general use contain platinum chloride or rhenium chloride supported on silica or silica–alumina. The catalyst pellets are generally supported on a bed of ceramic spheres about 30–40 cm deep. The spheres vary in size from about 2.5 cm in diameter on the bottom to about 9 mm in diameter at the top. Two types of Platforming processes are currently in use. The Semiregenerative Platforming process uses three or four reactors in series in which catalyst activity is regenerated at six to twelve month intervals. In the Continuous Platforming process catalyst activity is maintained by continuously withdrawing a small portion of catalyst and passing it through a regeneration tower where coke, a natural by-product of the reforming process, is burned off (45).

The product coming out of the reactor consists of excess hydrogen and a reformate rich in aromatics. Typically the dehydrogenation of naphthenes approaches 100% . From 0% to 70% of the paraffins are dehydrocyclized. The liquid product from the separator goes to a stabilizer where light hydrocarbons are removed and sent to a debutanizer. The debutanized platformate is then sent to a splitter where C_8 and C_9 aromatics are removed. The platformate splitter overhead, consisting of benzene, toluene, and nonaromatics, is then solvent extracted (46).

Aromatics Extraction. Even when rigorous reforming conditions are employed, the platformate splitter overhead usually contains significant amounts of nonaromatics that must be removed to provide an acceptable commercial benzene product. Numerous solvents are available for extraction of aromatics from an aromatic–aliphatic mixture. These include diethylene glycol (Udex process), *N*-methylpyrrolidinone (Arosolvan process), dimethylformamide (REDEX process), liquid SO_2 extraction (Edelanu process), tetramethylene sulfone *[126-33-0]* (Sulfolane process), and tetraethylene glycol (Tetra process, Union Carbide). The Udex process was the first solvent extraction process to find widespread usage prior to 1963. Since then, the Sulfolane process has become the most popular. This method, developed by Shell and licensed through UOP, was first reported in 1959 (47). A diagram of the Sulfolane extraction process is shown in Figure 2 (48). Feed is charged to a contactor for the countercurrent extraction of the aromatic components. Solvent from the extractor is charged to an extractive stripper. The stripper vapors are condensed and collected in a separator from which hydrocarbons are returned to the extractor. The stripper bottoms are charged to a recovery column that produces solvent-free aromatics. The aromatics are then fractionated to recover pure benzene.

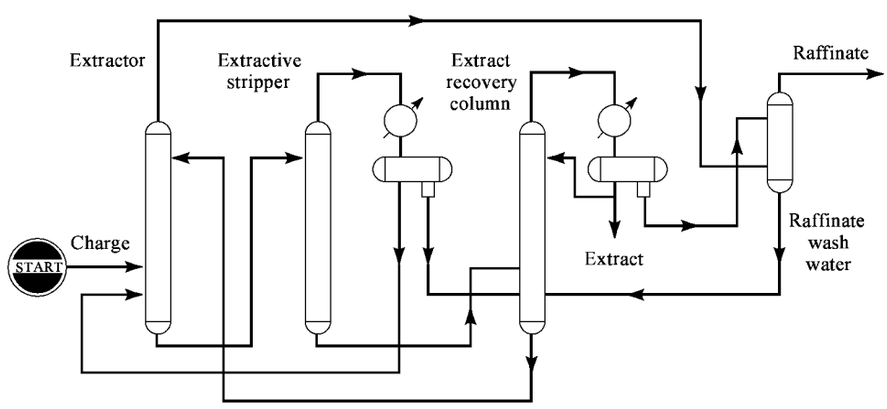


Fig. 2. Shell-UOP Sulfolane extraction process.

Courtesy Gulf Publishing Co., Houston, Tex. (48).

Toluene Hydrodealkylation. Benzene is produced from the hydrodemethylation of toluene under catalytic or thermal conditions. The main catalytic hydrodealkylation processes are Hydeal (UOP) and DETOL (Houdry) (49). Two widely used thermal processes are HDA (Arco and Hydrocarbon Research Institute) and THD (Gulf). These processes contribute 25–30% of the world's total benzene supply.

In catalytic toluene hydrodealkylation, toluene is mixed with a hydrogen stream and passed through a vessel packed with a catalyst, usually supported chromium or molybdenum oxides, platinum or platinum oxides, on silica or alumina (50). The operating temperatures range from 500–595°C

and pressures are usually 4–6 MPa (40–60 atm). The reaction is highly exothermic and the temperature is controlled by injection of quench hydrogen at several places along the reaction. Conversions per pass typically reach 90% and selectivity to benzene is often greater than 95%. The catalytic process occurs at lower temperatures and offers higher selectivities but requires frequent regeneration of the catalyst. Products leaving the reactor pass through a separator where unreacted hydrogen is removed and recycled to the feed. Further fractionation separates methane from the benzene product.

A typical catalytic hydrodealkylation scheme is shown in Figure 3 (49). The most common feedstock is toluene, but xylenes can also be used. Recent studies have demonstrated that C_9 and heavier monoaromatics produce benzene in a conventional hydrodealkylation unit in yields comparable to that of toluene (51). The use of feeds containing up to 100% of C_9–C_{11} aromatics increases the flexibility of the hydrodealkylation procedure which is sensitive to the price differential of benzene and toluene. When toluene is in demand, benzene supplies can be maintained from dealkylation of heavy feedstocks.

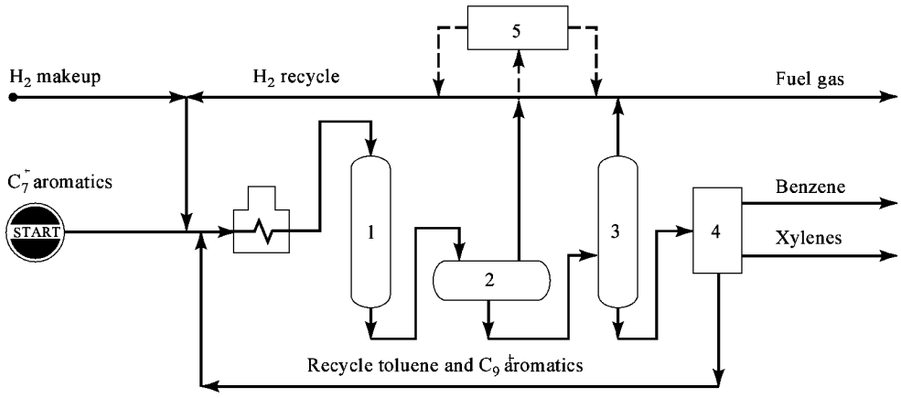


Fig. 3. DETOL hydrodealkylation process.

Courtesy Gulf Publishing Co., Houston, Tex. (49).

Transalkylation. Two molecules of toluene are converted into one molecule of benzene and one molecule of mixed xylene isomers in a sequence called transalkylation or disproportionation. Economic feasibility of the process strongly depends on the relative prices of benzene, toluene, and xylene. Operation of a transalkylation unit is practical only when there is an excess of toluene and a strong demand for benzene. In recent years, xylene and benzene prices have generally been higher than toluene prices so transalkylation is presently an attractive alternative to hydrodealkylation (see also BTX PROCESSING).

An example of toluene disproportionation, the Tatoray process, is shown in Figure 4 (52). Toluene and C_9 aromatics are mixed with liquid recycle and recycle hydrogen, heated to 350–530°C at 1–5 MPa (10–50 atm), and charged to a reactor containing a fixed bed of noble metal or rare earth catalyst. Hydrogen to feedstock mole ratios of 5:1 to 12:1 are typically required. Following removal of gases, the separator liquid is freed of light ends and the bottoms are then clay treated and fractionated to produce high purity benzene and xylenes. The yield of benzene and xylene obtained from this procedure is about 92% of the theoretical. Since the disproportionation is an equilibrium reaction, by varying the feedstock and experimental conditions the ratio of xylene to benzene can be changed.

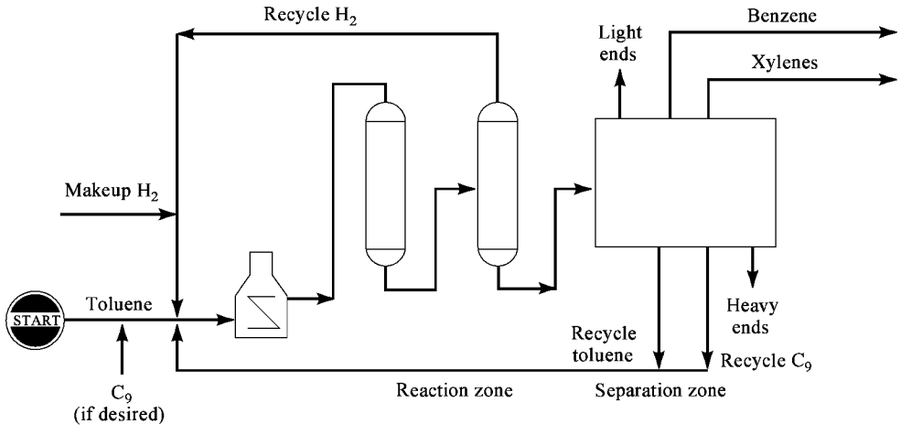


Fig. 4. Tatoray toluene disproportionation process.

Courtesy Gulf Publishing Co., Houston, Tex. (52).

Lyondell and Sun Oil Co. are the main producers of benzene by disproportionation. Fina Oil Co. of Texas has developed the Fina T2BX process for toluene disproportionation using a proprietary catalyst. The new catalyst is claimed to reduce hydrogen consumption and is suitable for feeds containing small amounts of moisture (53). A commercial production unit was started up in the fall of 1985.

Pyrolysis Gasoline. The steam cracking of heavy naphthas or light hydrocarbons such as propane or butane to produce ethylene yields a liquid by-product rich in aromatic content called pyrolysis gasoline, dripolene, or drip oil (54). A typical pyrolysis gasoline contains up to about 65% aromatics, about 50% of which is benzene. Approximately 30–35% of benzene produced worldwide is derived from pyrolysis gasoline. The remainder of the product is composed of mono- and diolefins. These olefinic substances are removed by a mild hydrogenation step. Following hydrogenation, the resulting pyrolysis gasoline is used in motor gasoline. Alternatively, pure benzene could be recovered from the pyrolysis gasoline by solvent extraction and subsequent distillation.

Miscellaneous Sources of Benzene. Benzene has been recovered from coal tar. The lowest boiling fraction is extracted with caustic soda to remove tar acids. The base washed oil is then distilled and further purified by hydrodealkylation.

The synthesis of aromatics from methane, and other light C_2, C_3, and C_4 hydrocarbons has been the subject of investigation since the 1980s. One recent example of this is British Petroleum's Cyclar process, modified with UOP's continuous catalyst regeneration technology (55). The process is claimed to produce high purity benzene, toluene, and xylenes from propane, isobutane, or *n*-butane feedstocks. The conversion of synthesis gas into aromatic hydrocarbons with metal zeolite catalysts such as ZSM-5 has also been reported (56). ZSM-5 has also been found to convert light paraffins, olefins, and naphthenes to aromatics and light gases (57). The name M2-Forming has been suggested to describe this recently discovered aromatization process. The production of aromatics and gasoline hydrocarbons from methanol has also received attention (58–60). The future may bring practical methods for

converting methane into benzene (61,62).

Economic Aspects

World benzene production rose to 6×10^6 t (1.8×10^9 gallons) in 1988 (63). The United States is the largest producer of benzene and accounts for about 30% of world production. The total annual U.S. production of benzene is shown in Table 4 which gives production figures from both petroleum- and coal-derived benzene. These figures show that benzene obtained from coal is steadily declining, and presently accounts for less than 5% of the total. Many useful statistics have been compiled (64).

Table 4. U.S. Production and Sales of Benzene[a], 10^3 t[b]

Year	Production		Sales
	Petroleum	Coal	
1974	4697	274	2634
1975	3203	217	1829
1976	4558	202	2129
1977	4580	216	2199
1978	4793	179	2528
1979	5383	203	3017
1980	5123	170	3831
1981	4368	105	2297
1982	3514	56	1825
1983	4093		2001
1984	4375		2154
1985	4259	116	1838
1986	4640	94	1787
1987	5295	160	2575
1988	5942	175	

[a] Ref. 64.

[b] To convert t to gallons, multiply by 300.

U.S. producers of benzene from petroleum and their approximate production capacities are shown in Table 5. These figures are inexact because the size of the market and instability of benzene prices causes frequent changes in capacity. Dow Chemical, with total annual benzene capacity of 8.3×10^5 t (250 million gallons) is the largest producer in the United States. Other companies with total domestic capacity of over 3.3×10^5 t (100 million gallons) per year are Amoco Corp., Lyondell, British Petroleum America, Chevron, Exxon Chemical, Occidental Petroleum, Shell Oil, and Mobil. These companies account for approximately 60% of total U.S. benzene capacity (65).

Table 5. U.S. Producers of Benzene from Petroleum and Annual Capacities[a]

Producers	Capacities, 10^3 t[b]
Continental United States	
American Petrofina Company, Inc.	214
Amoco Corp.	368
Aristech Chemical Corp.	150
Ashland Chemical Co.	191
British Petroleum America (incl. Sohio Oil Co.)	601
Champlin Refining and Chemicals, Inc.	183
Chevron Corp.	561
Citgo Petroleum Corp.	83
Coastal Corp.	116
Dow Chemical U.S.A.	835
Exxon Corp.	752
Hoechst-Celanese Corp.	50
Kerr-McGee Corp.	57
Koch Industries, Inc.	317
Lyondell Petrochemical Co.	474
Mobil Corp.	394
Occidental Petroleum Corp.	601
Phillips Petroleum	37
Salomon, Inc.	17
Shell Oil Co.	685
Sun Company, Inc.	301
Texaco Chemical	301
Unocal Corp.	63
USX Corp.	23
Virgin Islands and Puerto Rico	
Arochem International	301
Hess Oil Virgin Islands Corp.	257
Phillips Puerto Rico Core, Inc.	281
Total	*8063*

[a] As of Jan. 1, 1990 (65).

[b] To convert t to gal, multiply by 300.

U.S. petroleum benzene prices since 1974 are listed in Table 6 (64). Until 1978, benzene prices were relatively stable and through 1985 they increased considerably, peaking in 1981 because of the increased demand for aromatics in the gasoline pool. At that time, there was also a large surplus of low priced imported benzene and a softening of the ethylbenzene–styrene market. The decline of crude oil prices in 1986 caused a dramatic drop in domestic benzene prices. In 1987, U.S. benzene production increased 13.9% over 1986, and this rise was largely ascribed to a favorable export market for benzene derivatives

such as styrene (66). After midyear, benzene prices declined and then stabilized. In 1988, benzene prices hovered around $1.10 gallon ($330 t), and in February 1989, benzene prices rose to about $1.90 gallon ($570 t) on a contract basis (67). Prices for benzene weakened later in 1989. As of Oct. 14, 1991, spot benzene prices were listed at about $1.30 gallon ($390 t) (68).

Table 6. U.S. Petroleum Benzene Prices[a]

Year	Price	
	$ ton	¢ gallon
1974	239.5	80
1975	254.5	85
1976	239.5	80
1977	239.5	80
1978	209.6	70
1979	374.3	125
1980	494	165
1981	524	175
1982	464	155
1983	434	145
1984	428	143
1985	444	148
1986	275	90
1987	525	175
1988	329	110

[a] Ref. 64.

United States benzene trade data are shown in Table 7. From 1961 to 1970, the United States was a net exporter of benzene. After 1971, following a rapid growth of foreign benzene production, the amount of inexpensive benzene available from overseas sources brought the trade balance back to net imports. The trade balance was expected to fluctuate and a net import balance of 3.3*ndash*4.3 × 10^5 t (100–130 million gallons) was anticipated for 1990 (64).

Table 7. U.S. Benzene Trade[a], 10^3 t[b]

Year	Imports	Exports	Balance
1970	174.7	223.5	48.8
1971	256.2	142.3	113.9
1974	341.8	76.2	265.6
1975	234.9	60.1	174.8
1976	175.4	119.4	56.0
1977	208.1	116.1	92.0
1978	225.6	151.6	74.0
1979	233.9	59.0	174.9
1980	316.2	39.5	276.7
1981	443.4	119.3	324.1
1982	453.9	28.1	425.8
1983	492.7	36.6	456.2
1984	581.2	63.7	517.4
1985	499.1	38.0	461.1
1986	519.4	29.0	490.4
1987	535.5	115.2	420.3
1988	396.8	199.7	197.1

[a] Ref. 64

[b] To convert t to gal, multiply by 300.

Benzene production by various foreign countries is shown in Table 8 (69–72). As of 1987, the leading foreign producers of benzene were the Federal Republic of Germany, the United Kingdom, Japan, the Netherlands, and the USSR.

Until 1960, coal was the source material for almost all benzene produced in Europe. Petroleum benzene was first produced in Europe by the United Kingdom in 1952, by France in 1958, by the Federal Republic of Germany in 1961, and by Italy in 1962. Coal has continued to decline as a benzene source in Europe, and this is evident with the closure of coke ovens in Germany (73). Most of the benzene produced in Europe is now derived from petroleum or pyrolysis gasoline. In Europe, pyrolysis gasoline is a popular source of benzene because European steam crackers run on heavier feedstocks than those in the United States (73).

The main producers of benzene in Canada are the Nova Corp. of Alberta, Petro-Canada, Inc., and Shell Canada Ltd. These three companies have an annual capacity of 567,000 t. Most Canadian benzene is obtained from catalytic reformate, pyrolysis gasoline, and hydrodealkylation. Coal is not an important source of benzene in Canada.

The primary benzene producers in the United Kingdom are Shell Chemicals UK, Imperial Chemical Industries PLC, and BP Chemicals Ltd. These three companies have a combined annual capacity of over 1,100,000 t.

Some of the principal Japanese producers of benzene are Mitsubishi Petrochemical Co., Ltd., Nippon Steel Chemical Co., Ltd., Sanyo Petrochemical Ltd., and Idemitsu Kosan Ltd. Until 1967, the main source of Japanese benzene was coal-based. Today, approximately 40–45% of benzene production in Japan is based on pyrolysis gasoline (74), about 40% catalytic reformate, and the remainder coke oven light oil and thermal hydrodealkylation.

Table 8. Benzene Production by Various Countries[a], 10^3 t[b]

Country	1975	1980	1981	1982	1983	1984	1985	1986	1987
Belgium	38.5	39.1	46.7	41.0	40.8	33.9			
Brazil		308.5	316.6	357.8	435.8	490.0	514.9	524.1	601.7
Canada	248.0	560.0	566.5	519.0	580.0	548.7	691.3	635.4	719.6

Czechoslovakia	152.0	184.2	240.0	279.4	267.8	277.7	291.1	301.8	309.6
Federal Republic of Germany	691.2	919.1	921.6	1026.5	1335.8	1437.9		1533.4	1503.0
Finland		74.9	67.2	43.4					
France	295.1	547.3	500.2	513.9	626.7	601.0	632.8	603.6	654.0
Hungary	28.7	103.5	87.5	101.5	104.4	103.9	119.5	104.3	115.8
India	55.8	63.6	65.0	79.9	96.1	105.3	92.9	75.8	407.6
Italy	467.0	449.5	423.8	382.4	527.5	535.9	488.5	503.0	505.9
Japan	1608.2	2059.7	1898.8	1814.7	1938.0	2217.6	2279.4	2260.9	2417.7
(South) Korea, Republic of	8.4	92.9	109.3	120.0	158.9	171.0	215.9	301.4	339.0
Mexico	90.0	79.3	77.0	96.0	139.0	156.0	178.0	221.8	
Netherlands	729.0	732.0	744.0	772.0	1032.0	1091.4	975.0	980.0	1196.0
Romania	125.0	122.0	150.0	161.0	204.0	207.0	185.0	203.0	226.0
Spain	197.4	212.0	204.7	174.6	194.1	229.4	258.0	231.3	265.2
Turkey	2.3	13.4	14.3	12.0	9.8	13.0	13.0	54.7	88.0
United Kingdom	582.0	825.5	752.0	569.6	725.9	754.7	834.9	860.4	911.6
United States	3459.4	6497.0	4343.3	3492.5	4093.5	4375.5	4259.2	4520.8	5231.3
USSR	1427.0	1644.0	1698.0	1690.0	1853.0	1956.3	1971.4	2138.7	2168.0
Yugoslavia	44.0	18.2	40.3	21.2	25.4	25.1	19.0	20.1	18.9

[a] Refs. 69–72.

[b] To convert t to gal, multiply by 300.

The principal producers of benzene in the Netherlands are Dow Chemical Nederland BV, Exxon Chemical Holland, and DSM NV Plastics Division. These three companies have a combined annual capacity of about 955,000 t.

Table 9 shows benzene imports from various foreign countries for 1983–1988 (64,75). Since 1971 the United States has been a net importer of benzene, and the quantities imported have been steadily increasing. Canada, the Netherlands, and the United Kingdom accounted for almost 70% of all benzene imported into the United States in 1988.

Table 9. U.S. Imports of Benzene from Various Foreign Countries[a], 10^3 t[b]

Country	1983	1984	1985	1986	1987	1988
Argentina	59.2	65.6	56.0	26.6	34.0	11.0
Brazil	61.7	92.4	51.4	69.3	53.0	25.7
Canada	114.0	87.4	81.9	64.3	83.5	115.6
Colombia	10.8	2.5	9.2	8.8	10.9	
Federal Republic of Germany	7.3	13.3		5.2	14.5	6.0
France	10.8	10.9	5.1	12.0	10.3	9.7
Israel	3.0	3.9		2.8	4.9	
Italy	49.9	29.0	20.6	5.7	2.9	
Japan	24.8	57.2	89.4	106.6	70.0	43.8
Mexico	4.2	36.6	8.8	4.4	5.5	
the Netherlands	96.5	146.9	108.9	127.4	132.4	83.4
Spain	4.7		2.8		0.42	
Switzerland	3.1			8.5	10.3	3.2
United Kingdom	27.3	1.5	25.1	16.7	67.2	76.8
USSR		7.7	13.7		7.3	15.0

[a] Refs. 64, 75.

[b] To convert t to gal, multiply by 300.

Specifications, Standards, and Test Methods

Several different grades of benzene are commercially available. The most common grades are benzene 535, benzene 485 (nitration grade), benzene 545, and thiophene-free benzene. Specifications and the corresponding ASTM test procedures for these various types are shown in Table 10 (76). ACS specifications for reagent grade benzene are shown in Table 11 (77). Industrial-grade benzene is used primarily in applications that are insensitive to impurities. Nitration-grade benzene is a high quality product used for preparing nitrobenzene and derivatives. Thiophene-free benzene is used as a reagent in ASTM standards and is specially treated to remove thiophene. Thiophene and organic sulfur compounds foul many catalysts used in reactions of benzene.

Table 10. Specifications for Commercial Grades of Benzene[a]

ASTM test	Benzene 535[b]	Benzene 485[c]	Industrial-grade[d]
appearance	clear liquid, free from sediment or haze at 18–24°C	clear liquid, free from sediment or haze at 18–24°C	clear liquid, free from sediment at 18–24°C
relative density, 14.56–15.56°C, D3505	0.8820–0.8860	0.8820–0.8860	0.875–0.886
density, 20°C, g cm^{3}, D4052	0.8780–0.8820	0.8780–0.8820	0.871–0.882
color pt-co scale, D1209	20 max	20 max	20 max
total distillation range, 101.3 kPa[e], D850	1.0°C max, including the temperature of 80.1°C	1.0°C max, including the temperature of 80.1°C	2.0°C max, including the temperature of 80.1°C
solidification point, D852	5.35°C (anhydrous)	not lower than 4.85°C (anhydrous)	
acid wash color, D848	1 max	2 max	3 max
acidity, D847	none detected	none detected	none detected
H_2S and SO_2, D853	none detected	none detected	none detected
thiophene, D1685	1 mg kg max		
copper corrosion, D849	pass	pass	copper strip shall not show iridescence, a gray or black

		deposit, or discoloration
nonaromatics, D2360	0.15 wt % max	

[a] Ref. 76.
[b] ASTM D2359-85a.
[c] Nitration-grade, ASTM D835-85.
[d] ASTM D836-84.
[e] To convert kPa to mm Hg, multiply by 7.5.

Table 11. Specifications for ACS Reagent-Grade Benzene[a]

Specification	Value
color (APHA)	not more than 10
boiling range	entirely within 1.0°C range including 80.1°C ± 0.1°C
freezing point	not below 5.2°C
residue after evaporation	not more than 0.001%
substances darkened by sulfuric acid	to pass test
thiophene	to pass test (limit ≈ 1 ppm)
sulfur compounds (as S)	not more than 0.005%
water	not more than 0.05%

[a] Ref. 77.

The purity of benzene marketed for most laboratory purposes is usually greater than 95.5% with the principal impurities being toluene and other hydrocarbons with boiling points similar to that of benzene. Methods used to assess the quality of benzene include determination of density, boiling point, distillation characteristics, and specific gravity. Benzene of high purity samples is conveniently measured by freezing point, as outlined in ASTM D1016. The acid wash test consists of shaking a mixture of 96% sulfuric acid with benzene and comparing the color of the (lower) acid layer with a set of color standards. Other qualitative tests include those for SO_2 and H_2S determination. The copper strip corrosion test indicates the presence of acidic or corrosive sulfur impurities. The test for thiophene is colorimetric.

Analysis. The infrared (ir), ultraviolet (uv), and nuclear magnetic resonance (nmr) spectra are distinct and characteristic for benzene and are widely used in analysis (78–80). Benzene also produces diagnostic ions in the mass spectrum (81,82) (see ANALYTICAL METHODS).

The identification of benzene is most easily carried out by gas chromatography (83). Gas chromatographic analysis of benzene is the method of choice for determining benzene concentrations in many diverse media such as petroleum products or reformate, water, soil, air, or blood. Benzene in air can be measured by injection of a sample obtained from a syringe directly into a gas chromatograph (84).

In recent years, gas chromatograph–mass spectrometer (gc–ms) systems have become popular for analyzing trace amounts of benzene (85). The gc–ms method gives higher accuracy and precision than conventional gc methods because components are identified by molecular weight, even when benzene may overlap with other compounds. With multichanneled, double-focusing instruments, detection limits of 0.1 ppb in air or breath samples are claimed by a selective ion monitoring gas chromatography–mass spectrometry procedure (sim–gc–ms) (86).

Rapid, simple, qualitative methods suitable for determining the presence of benzene in the workplace or surroundings have been utilized since the 1930s. Many early tests offered methods for detection of aromatics but were not specific for benzene. A straightforward test allowing selective detection of benzene involves nitration of a sample to *m*-dinitrobenzene and reaction of the resultant ether extract with an ethanolic solution of sodium hydroxide and methyl ethyl ketone (2-butanone), followed by the addition of acetic acid to eliminate interferences from toluene and xylenes. Benzene imparts a persistent red color to the solution (87). The method is claimed to be sensitive to concentrations as low as 0.27 ppm benzene from 10 mL air samples.

Benzene reacts with concentrated sulfuric acid and formaldehyde to produce a brown precipitate. A similar reaction occurs with ferrous sulfate and hydrogen peroxide. The resulting brown solid is dissolved in nitric acid for comparison with color standards.

Colorimetric methods have led to the development of visual devices for measurement of benzene concentration. These visual detection tubes have been popular since the 1960s and have provided a simple and reliable method for evaluating ambient aromatic vapor contamination. These products are available from a number of manufacturers such as Drager (Lubeck, Germany), Gastec (Tokyo, Japan), Kitagawa (Kawasaki, Japan), DuPont (Wilmington, Delaware, USA), and 3M (St. Paul, Minnesota, USA) (85).

Various types of detector tubes have been devised. The NIOSH standard number S-311 employs a tube filled with 420–840 μm (20 40 mesh) activated charcoal. A known volume of air is passed through the tube by either a handheld or vacuum pump. Carbon disulfide is used as the desorbing solvent and the solution is then analyzed by gc using a flame-ionization detector (88). Other adsorbents such as silica gel and desorbents such as acetone have been employed. Passive (diffuse samplers) have also been developed. Passive samplers are useful for determining the time-weighted average (TWA) concentration of benzene vapor (89). Passive dosimeters allow permeation or diffusion-controlled mass transport across a membrane or adsorbent bed, ie, activated charcoal. The activated charcoal is removed, extracted with solvent, and analyzed by gc. Passive dosimeters with instant readout capability have also been devised (85).

Determination of benzene in air samples has been achieved by bubbling contaminated air through various solvents, followed by uv or ir analysis of the solution (90). Methods for identifying benzene in soil, water, and biological media are further described in references 84 and 85.

Handling and Shipping

Manufacturers of benzene are required by federal law to publish Material Safety Data Sheets (MSDS) that describe in detail the procedures for its safe handling. Benzene is classified as a flammable liquid and should be stored away from any potential source of ignition. Fire and explosion hazard data for benzene are shown (91).

flash point, closed cup, °C	11
autoignition temperature, °C	560
flammable limits, vol % in air	1.4 (lower)–8.0 (upper)

Benzene is shipped by rail tank cars, trucks, barges, and tankers. Because of the flammability, toxicity, and volatility of benzene, transfers from one vessel to another are conducted in closed systems. Metal tanks and storage containers should be grounded during transfers. Smaller quantities of benzene are routinely shipped in steel or glass containers. Benzene should be handled only where adequate ventilation is provided; protective clothing and self-contained respirators are recommended. Labeling, packaging, and domestic or international transportation of benzene must comply with regulations described in the *Code of Federal Regulations* (CFR) Title 49. OSHA regulations are described in 29 CFR, Parts 1501, 1502, and 1503. New exposure limits for

benzene are published in 29 CFR, Part 1910.1028.

Environmental Considerations

Benzene is classified as a hazardous waste by the EPA under subtitle C of the Resource and Recovery Act (RCRA) (92). Effective Sept. 25, 1990, solid wastes containing more than 0.5 mg mL benzene must be treated in accordance with applicable RCRA regulations. Benzene is also subject to annual reporting of environmental releases as described in Section 313 of the Emergency and Community Right to Know Act of 1986 (93). Benzene emissions and effluent streams from petroleum refineries or benzene processing plants are also subject to strict federal regulations. Federal waste management procedures must be complied with for any industrial process involving manufacture, transport, treatment, or disposal of benzene. A complete description of the new EPA regulations concerning benzene and other hazardous wastes is found in the *Federal Register* (94). Further information regarding the handling and disposal of toxic or hazardous wastes is in the CFR, vol. 40.

Health and Safety

At room temperature and atmospheric pressure benzene is sufficiently vaporized to pose an inhalation hazard. Benzene is a toxic substance which can produce both acute and chronic adverse health effects. It is generally recognized that prolonged or repeated exposure to benzene can result in serious damage to the blood-forming elements. The first indications of benzene toxicity during occupational exposure were reported in Sweden in 1897 (95). By the early 1900s it was clear that humans chronically exposed to benzene suffered bone marrow damage.

Prolonged or repeated exposure to benzene vapor results in blood dyscrasias including lympho-, thrombo-, and pancytopenia, a decrease in all types of circulating blood cells (96–98). The decrease in blood components, caused by the action of benzene on bone marrow, is referred to as aplastic anemia and is the disease most commonly associated with benzene exposure (98). Cases of benzene poisoning resulting in hematological disturbances have been reported from repeated exposures to amounts as low as 60 ppm (99). In the early stages of chronic exposure the blood changes are variable, but as the disease becomes established a decrease in polymorphonuclear leucocytes and a relative lymphocytosis are found (100). If benzene exposure is stopped, the blood changes may or may not be reversed, and the blood morphology may require several years to return to normal (101).

A less frequent, but more serious, health complication resulting from chronic benzene exposure is the development of leukemia. The relationship between benzene and leukemia was suggested in the late 1920s. By the late 1930s, 10 cases of leukemia linked to benzene had been documented worldwide. A number of clinical case reports and several epidemiological studies followed and by the late 1970s benzene was clearly-recognized as a carcinogen (leukemogen). Acute myelogenous leukemia (AML) is the most common form of the disease associated with benzene exposure (95,102,103). It is believed that most, if not all, benzene-induced leukemias are preceded by pancytopenia or aplastic anemia (104) followed by a latency period of at least several years. Currently, the long-term prognosis for AML is poor and the outcome is usually fatal. Benzene has been linked to other, less common forms of leukemia, including lymphoid, myeloblastic, erythroblastic, and the hairy-cell varieties (105,106).

Neither the mechanism by which benzene damages bone marrow nor its role in the leukemia process are well understood. It is generally believed that the toxic factor(s) is a metabolite of benzene (107). Benzene is oxidized in the liver to phenol *[108-95-2]* as the primary metabolite with hydroquinone *[123-31-9]*, catechol *[120-80-9]*, muconic acid *[505-70-4]*, and 1,2,4-trihydroxybenzene *[533-73-3]* as significant secondary metabolites (108). Although the identity of the actual toxic metabolite or combination of metabolites responsible for the hematological abnormalities is not known, evidence suggests that benzene oxide, hydroquinone, benzoquinone, or muconic acid derivatives are possibly the ultimate carcinogenic species (96,103,107–112).

Recently, the myelotoxicity has been proposed to occur through initial conversion of benzene to phenol and hydroquinone in the liver, selective accumulation of hydroquinone in the bone marrow, followed by conversion of hydroquinone to benzoquinone via bone marrow myeloperoxidase. Benzoquinone is then proposed to react with macromolecules disrupting cellular processes (108).

Benzene is rapidly absorbed from the lungs into the bloodstream. Studies on the inhalation of benzene have given a retention at rest of about 50% (107). The half-life for benzene disappearance in the body is about 0.4–1.6 h (113). Benzene accumulates in fatty tissues and continues to be excreted long after exposure. In one particular study, volunteers were exposed to 200 ppm benzene per hour over an 8-h workday for five days. After the fifth day of exposure, the volunteers exhaled twice as much benzene as on the first day of exposure (114). In another study, it was observed that 26% of absorbed benzene was exhaled unmetabolized and was excreted in the urine as 61% phenol, 6.4% catechol, and 2% hydroquinone (115). Because benzene is oxidized mainly to phenol, the urinary phenol test is a widely used method for detecting benzene exposure. Urinary phenol content of nonoccupationally exposed subjects does not usually exceed 20 mg L (116). Determining the ratio of inorganic to organic sulfate in urine is no longer recommended for evaluating benzene exposure because of its recognized low specificity to phenol (117).

Aplastic anemia and leukemia are not the only health effects ascribed to benzene exposure. A number of recent studies have associated benzene exposure with chromosomal changes (aberrations) (118). Other studies have shown abnormalities in porphyrin metabolism and decrease in leucocyte alkaline phosphatase activity in apparently healthy workers exposed to 10–20 ppm benzene (119,120). Increases in leukoagglutinins, as well as increases in blood fibrinolytic activity, have also been reported and are believed to be responsible for the persistent hemorrhages in chronic benzene poisoning (121,122).

Inhalation of 3,000 ppm benzene can be tolerated for 0.5–1 h; 7,500 ppm causes toxic effects in 0.5–1 h; and 20,000 ppm is fatal in 5–10 min (123). The lethal oral dose for an adult is approximately 15 mL (124). Repeated skin contact is reported to cause drying, defatting, dermatitis, and the risk of secondary infection if fissuring occurs.

In chronic benzene intoxication, mild poisoning produces headache, dizziness, nausea, stomach pain, anorexia, and hypothermia. In severe cases, pale skin, weakness, blurred vision, and dyspnea occur on exertion. Hemorrhagic tendencies include petechia, easy bruising, and bleeding gums. Bone marrow depression produces a decrease in circulating peripheral erythrocytes and leucocytes (101). Fatalities from chronic exposure show at autopsy severe bone marrow aplasia, and necrosis or fatty degeneration of the heart, liver, and adrenals (125).

Acute benzene poisoning results in CNS depression and is characterized by an initial euphoria followed by staggered gait, stupor, coma, and convulsions. Exposure to approximately 4000 ppm benzene results in complete loss of consciousness. Insomnia, agitation, headache, nausea, and drowsiness may persist for weeks after exposure (126). Continued inhalation of benzene to the point of euphoria has caused irreversible encephalopathy with tremulousness, emotional lability, and diffuse cerebral atrophy (125). In deaths arising from acute exposure, respiratory tract infection, hypo- and hyperplasia of sternal bone marrow, congested kidneys, and cerebral edema have been found at autopsy.

Treatment for acute exposure to benzene vapor involves removing the subject from the affected area, followed by artificial respiration with oxygen; intubation and cardiac monitors may be necessary for severe acute exposures (125,127). Because of its low surface tension, benzene poses a significant aspiration hazard if the liquid enters the lungs. Emesis is indicated in alert patients if more than 1 mL of benzene per kg of body weight has been ingested and less than two hours have passed between ingestion and treatment (127).

Treatment for chronic benzene poisoning is supportive and symptomatic, with chemotherapy and bone marrow transplants as therapeutic agents for leukemia and aplastic anemia (127).

Regulations

Because of the potential hazards associated with benzene, exposure to benzene in the workplace has been heavily regulated in the United States. Benzene is considered one of the approximately 40 known human carcinogens. Benzene is listed as an ACGIH suspected human carcinogen, an NTP human carcinogen, and an IARC human carcinogen. Six foreign countries, including Germany, Italy, Japan, Sweden, and Switzerland, recognize benzene as a carcinogen (95). In the United States, the earliest limit on benzene exposure was recommended in 1927 at 100 ppm (128). Over the decades the upper allowable limits were reduced to 50, 35, then 25 ppm (95). Fifteen countries have been reported to limit occupational exposure to benzene by regulation or recommended guideline. These occupational exposure limits are shown in Table 12 (129).

Table 12. National Exposure Limits for Benzene[a]

Country	Year	Concentration[b], ppm	Status
Australia	1978	10	guideline
Belgium	1978	10	regulation
Czechoslovakia	1976	160	regulation
		256[c]	
Finland	1975	10	regulation
Hungary	1974	64	regulation
Italy	1978	10	guideline
Japan	1978	25[d]	guideline
the Netherlands	1978	10	guideline
Poland	1976	64[d]	regulation
Romania	1976	160[e]	regulation
Sweden	1978	5	guideline
		10[f]	
Switzerland	1978	2	regulation
United States	1987	1	regulation
USSR	1980	16[d]	regulation
Yugoslavia	1971	15[d]	regulation

[a] Ref. 129.
[b] TWA, unless otherwise noted.
[c] 10 min ceiling.
[d] Ceiling.
[e] Maximum.
[f] 15 min maximum.

In 1971 the OSHA standard for benzene (20 CFR, Part 1910.0000) adopted a permissible exposure limit (PEL) of 10 ppm benzene measured as an 8-h TWA. In October of 1976 NIOSH updated its earlier criteria document on benzene and recommended that OSHA lower the benzene exposure standard from 10 to 1 ppm. This proposed implementation was blocked by the United States Supreme Court in 1980 on the basis of insufficient evidence linking benzene to cancer deaths. By the mid-1980s convincing evidence of the carcinogenicity of benzene appeared through animal studies which justified reconsideration of the 1 ppm PEL (130).

Effective Dec. 10, 1987, the existing standard for benzene was amended under OSHA (29 CFR, Part 1910.1028). The revised standard reduced the permissible exposure limit from 10 ppm (32 mg m^3) to 1 ppm (3.2 mg m^3) in an 8-h TWA. The short term exposure limit (STEL) of 5 ppm was set over a 15 min period. The standard also established action level requirements for exposure over 0.5 ppm.

Further, this standard provides for methods of compliance, personal protective equipment, adequate communication of benzene hazards to employees, regulated areas, and medical surveillance of workers who are or may be exposed to benzene. Any employee routinely exposed to benzene should, in addition to wearing protective equipment, receive periodic blood tests.

Uses

In the early part of the twentieth century, benzene was used as a universal solvent and degreaser and found widespread use throughout the rubber industry in the manufacture of tires. By the late 1920s, following reports of deaths due to benzene exposure, it was largely replaced by toluene and aliphatic solvents (131).

Before World War II, the largest market for benzene was in gasoline blending to improve octane ratings. After 1950, benzene in gasoline was largely replaced with tetraethyllead. In recent years, with the recognition of the hazards of lead in the environment, the EPA has limited the amount of lead in gasoline to 0.1 g leaded gallon (132). In addition, the EPA has suggested limits for benzene content of gasoline. The California Air Resources Board (CARB) has proposed limits on benzene in motor gasoline of 0.8 vol % after September, 1990. It is possible in the future that other aromatics in gasoline, especially xylenes, will face similar restrictions. Benzene content of U.S. motor gasoline currently ranges from approximately 0.1 to 4.4 vol % (133).

Benzene is still used extensively as a gasoline component in Europe and many countries do not limit the benzene content (134). Exceptions are Austria, Norway, Sweden, and Switzerland, which set the maximum at 5.0 vol % (134). Over 90% of European motor gasolines are below the 5.0 vol % limit set by these countries. It is likely that benzene content of European gasoline will be further reduced in the future.

Benzene is now used primarily as an intermediate in the manufacture of industrial chemicals. Approximately 95% of U.S. benzene is consumed by industry for the preparation of polymers, detergents, pesticides, pharmaceuticals, and allied products.

Estimates of benzene consumption for nonfuel uses are shown in Table 13 (135). Benzene consumption worldwide is dominated by the production of three main derivatives, styrene, cumene, and cyclohexane, which account for nearly 90% of the total.

Table 13. U.S. Use Pattern for Benzene, 1988[a]

Use	Total consumption, %
ethylbenzene	51.8
cumene	21.7
cyclohexane	14.4
nitrobenzene	4.9
chlorobenzenes	2.1
linear detergent alkylate	1.9
maleic anhydride	0.0
other	3.2

[a] Ref. 135.

Benzene is alkylated with ethylene to produce ethylbenzene, which is then dehydrogenated to styrene, the most important chemical intermediate derived from benzene. Styrene is a raw material for the production of polystyrene and styrene copolymers such as ABS and SAN. Ethylbenzene accounted for nearly 52% of benzene consumption in 1988.

Benzene is alkylated with propylene to yield cumene (qv). Cumene is catalytically oxidized in the presence of air to cumene hydroperoxide, which is decomposed into phenol and acetone (qv). Phenol is used to manufacture caprolactam (nylon) and phenolic resins such as bisphenol A. Approximately 22% of benzene produced in 1988 was used to manufacture cumene.

Benzene is hydrogenated to cyclohexane. Cyclohexane is then oxidized to cyclohexanol, cyclohexanone, or adipic acid (qv). Adipic acid is used to produce nylon. Cyclohexane manufacture was responsible for about 14% of benzene consumption in 1988.

Nitration of benzene yields nitrobenzene, which is reduced to aniline, an important intermediate for dyes and pharmaceuticals. Benzene is chlorinated to produce chlorobenzene, which finds use in the preparation of pesticides, solvents, and dyes.

About 2% of benzene consumed in 1988 was used for the manufacture of straight-chain or branched-chain detergent alkylate. Linear alkane sulfonates (LAS) are widely used as household and laundry detergents.

Prior to 1975, benzene was catalytically oxidized to produce maleic anhydride, an intermediate in synthesis of polyester resins, lubricant additives, and agricultural chemicals. By 1986 all commercial maleic anhydride was derived from oxidation of *n*-butane. It is expected that *n*-butane will remain the feedstock of choice for both economic and environmental reasons.

Minor Uses. Small amounts of benzene find use in production of benzene-sulfonic acid. *m*-Benzenedisulfonic acid is used to produce resorcinol *[108-46-3]*, C H O_2, (1,3-dihydroxybenzene). Benzene is thermally dimerized to yield biphenyl *[92-52-4]*, $C_{12}H_{10}$. Benzene can also be converted into *p*-diisopropylbenzene *[100-18-5]*, $C_{12}H_{18}$, which is oxidized to hydroquinone (1,4-dihydroxybenzene), a useful antioxidant. Because of its well-recognized toxicity, little benzene is employed for solvent purposes, and then only when no suitable substitutes are available.

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BENZENESULFONIC ACID.

See SULFONIC ACIDS.

BENZINE.

See FEEDSTOCKS, PETROCHEMICALS AND FEEDSTOCKS.

BENZOIC ACID

Benzoic acid *[65-85-0]*, C_6H_5COOH, the simplest member of the aromatic carboxylic acid family, was first described in 1618 by a French physician, but it was not until 1832 that its structure was determined by Wuhler and Liebig. In the nineteenth century benzoic acid was used extensively as a medicinal substance and was prepared from gum benzoin. Benzoic acid was first produced synthetically by the hydrolysis of benzotrichloride. Various other processes such as the nitric acid oxidation of toluene were used until the 1930s when the decarboxylation of phthalic acid became the dominant commercial process. During World War II in Germany the batchwise liquid-phase air oxidation of toluene became an important process.

In the United States all other processes have been completely phased out and virtually all benzoic acid is manufactured by the continuous liquid-phase air oxidation of toluene. In the late 1950s and the early 1960s both Dow Chemical and Snia Viscosa constructed facilities for liquid-phase toluene oxidation because of large requirements for benzoic acid in the production of phenol and caprolactam. Benzoic acid, its salts, and esters are very useful and find application in medicinals, food and industrial preservatives, cosmetics, resins, plasticizers, dyestuffs, and fibers.

Occurrence

Benzoic acid in the free state, or in the form of simple derivatives such as salts, esters, and amides, is widely distributed in nature. Gum benzoin (from *styrax benzoin*) may contain as much as 20% benzoic acid in the free state or in combinations easily broken up by heating. Acaroid resin (from *Xanthorrhoea hastilis*) contains from 4.5 to 7%. Smaller amounts of the free acid are found in natural products including the scent glands of the beaver, the bark of the black cherry tree, cranberries, prunes, ripe cloves, and oil of anise seed. Peru and Tolu balsams contain benzyl benzoate; the latter contains free benzoic acid as well. The urine of herbivorous animals contains a small proportion of the glycine derivative of benzoic acid, hippuric acid *[495-69-2]*, ($C_6H_5CONHCH_2COOH$). So-called natural benzoic acid is not known to be available as an item of commerce.

Properties

Selected physical properties of benzoic acid are given in Table 1, solubilities in water in Table 2, solubilities in various organic solvents in Table 3, and vapor pressures in Table 4.

Table 1. Physical Properties of Benzoic Acid

molecular formula	$C_7H_6O_2$
mp, °C	122.4
bp, at 101.3 kPa,[a] °C	249.2
density	
solid, d_4^{24}	1.316
liquid, d_4^{180}	1.029
refractive index, n_D[b], liquid	1.504
viscosity at 130°C, mPa·s (cP)	1.26
surface tension at 130°C, mN/m (dyn/cm)	31
specific heat, J/(g·°C)	
solid	1.1966
liquid	1.774
heat of fusion, J/g[c]	147
heat of combustion, kJ/mol[c,d]	3227
heat of formation at 26.16°C, kJ/mol[c], solid[e]	385
heat of vaporization,[f] at 140°C, J/g[c]	534
at 249°C, J/g[c]	425
dissociation constant, K_a, at 25°C	6.339×10^{-5}
flash point, °C	121–131
autoignition temperature, °C, in air	573
pH of saturated aqueous solution at 25°C	2.8

[a] To convert kPa to atm, divide by 101.3.

[b] At 131.9°C.

[c] To convert J to cal, divide by 4.184.

[d] Refs. 1, 2.

[e] Ref. 3.

[f] Ref. 4.

Table 2. Solubilities in Water

Temperature, °C	g 100 g[a]	Temperature, °C	g 100 g[a]
0°C	0.17	50°C	0.85
10°C	0.21	60°C	1.20
20°C	0.29	70°C	1.77
25°C	0.34	80°C	2.75
30°C	0.42	90°C	4.55
40°C	0.60	95°C	6.80

[a] Grams benzoic acid per 100 g water.

Table 3. Solubilities in Nonaqueous Solvents at 25°C

Solvent	g 100 g[a]	Solvent	g 100 g[a]
acetone	55.6	ethyl ether	40.8
benzene	12.2	hexane, 17°C	0.9
carbon tetrachloride	4.1	methanol, 23°C	71.5
chloroform	15.0	toluene	10.6
ethanol (abs)	58.4		

[a] Grams benzoic acid per 100 g solvent.

Table 4. Vapor Pressure of Benzoic Acid[a]

Temperature, °C	Pressure, kPa[b]	Temperature, °C	Pressure, kPa[b]
96.0°C	0.13	172.8°C	8.0
119.5°C	0.67	186.2°C;	13.3
132.1°C	1.33	205.8°C	26.6
146.7°C	2.66	227.0°C	53.3
162.6°C	5.32	249.2°C	101.3

[a] Ref. 5.

[b] To convert kPa to mm Hg, multiply by 7.5.

In its chemical behavior benzoic acid shows few exceptional properties; the reactions of the carboxyl group are normal, and ring substitutions take place as would be predicted.

Manufacture

Benzoic acid is almost exclusively manufactured by the cobalt catalyzed liquid-phase air oxidation of toluene *[108-88-3]*. Large-scale plants have been built for benzoic acid to be used as an intermediate in the production of phenol (by Dow Chemical) and in the production of caprolactam (by Snia Viscosa) (6–11).

The basic process usually consists of a large reaction vessel in which air is bubbled through pressurized hot liquid toluene containing a soluble cobalt catalyst as well as the reaction products, a system to recover hydrocarbons from the reactor vent gases, and a purification system for the benzoic acid product.

Reaction. Typical liquid-phase toluene oxidizer reaction conditions may be as follows:

reactor pressure	200–700 kPa (~2–7 atm)
reactor temperature	136–160°C
cobalt catalyst concentration	25–1000 ppm
reactor benzoic acid concentration	10–60 wt %

A number of different cobalt salts have been used in the oxidation of toluene, the most common being cobalt acetate *[71-48-7]*, cobalt naphthenate, and cobalt octoate *[1588-79-0]*.

Manganese has also been suggested as a co-catalyst. There is some indication that manganese adversely affects the reactor equilibrium such that the coproduction of benzaldehyde *[100-52-7]* suffers. Those benzoic acid producers who also produce benzaldehyde do not use manganese in their systems.

Catalysts other than the above cobalt salts have been considered. Several patents suggest that cobalt bromide gives improved yields and faster reaction rates (12–16). The bromide salts are, however, very corrosive and require that expensive materials of construction, such as Hastalloy C or titanium, be used in the reaction system. Only one facility, located in the UK, is believed to utilize cobalt bromide catalyst in the production of benzoic acid.

Purification. Small amounts of reaction by-products are produced during the liquid-phase oxidation of toluene. These by-products include acetic and formic acids, benzene, benzaldehyde, benzyl alcohol, aliphatic benzyl esters such as benzyl formate and benzyl acetate, biphenyl, 2-, 3-, and 4-methylbiphenyls, and phthalic acid. Of these only benzaldehyde and benzene *[71-43-2]* are currently separated commercially.

The recovery and purification of benzoic acid from a liquid-phase toluene oxidizer may involve distillation alone or it may involve a combination of distillation followed by extraction and crystallization.

In either case, the initial distillation involves separating toluene and any material lower boiling than benzoic acid and recycling those low boilers to the toluene oxidizer. The benzoic acid and higher boiling fractions are then distilled and or subjected to an extraction and crystallization process to

produce the desired product.

The toluene to phenol production plants have a significant advantage regarding cost in producing benzoic acid. These plants produce an industrial-grade benzoic acid by distillation, and that industrial-grade product then serves as the feedstock to the phenol plant as well as to the technical and USP FCC production facilities. Utilizing distillation or extraction and crystallization, these plants reject undesirable impurities, such as the methyl biphenyls, into the phenol reactors in dilute concentrations with benzoic acid. These impurities are actually beneficial to the phenol plant, assisting in the removal of reaction tars. Stand-alone benzoic acid producers are forced to spend large amounts of capital and or suffer significant unit ratio penalties to produce a similar product.

In addition to the presence of organic trace impurities, the color and color stability of the benzoic acid are often important to customers. Various techniques are utilized to improve color and color stability. Most if not all of these are considered trade secrets.

The USP FCC grade of benzoic acid is usually produced by extraction and crystallization, although distillation has also been used. In the extraction–crystallization process, toluene, water, and methanol have all been used and each is capable of producing a high quality benzoic acid product.

Hydrocarbon Recovery. Toluene is typically recovered from the oxidizer vent gases through the use of refrigeration followed by activated carbon adsorption.

Vapor-phase oxidation of toluene to produce benzoic acid and benzaldehyde has been tried utilizing several different catalysts, but yields are low and the process cannot compete with the liquid-phase process (see BENZALDEHYDE). Other processes for the production of benzoic acid are presently of little commercial importance.

Economic Aspects

The growth of demand for benzoic acid is expected to increase at a rate of between 1 and 2% per year (17). Glycol dibenzoate plasticizers have been growing at close to 10% annually for the past several years, in part due to environmental concerns with regard to phthalate plasticizers (qv). The growth of the diet soft drink market has increased the demand for sodium and potassium benzoates (17).

All of the benzoic acid producers in the United States employ the liquid-phase toluene air oxidation process. As toluene becomes more important in the gasoline pool as an octane booster, the benzoic acid producers have to compete with gasoline marketers for the available toluene. If the attractiveness of toluene as an octane booster continues, the cost of producing benzoic acid will most likely increase.

The principal North American producers of benzoic acid and their estimated production capacities are as follows (17):

Producer	*Capacity, t/yr*
Kalama Chemical, Kalama, Washington	80,000
Chatterton Petrochemical, Delta, B.C., Canada	65,000
Velsicol Chemical, Chattanooga, Tennessee	32,500

The bulk of this benzoic acid production capacity is consumed internally by the producers. Kalama and Chatterton convert over half of their production to phenol. A large portion of Velsicol's benzoic acid production is utilized in the manufacture of glycol dibenzoate plasticizer esters.

Specifications, Analysis, Packaging, and Shipment

Benzoic acid is available in industrial and technical grades, and in grades meeting the specifications of the *United States Pharmacopeia* (18), the *Food Chemicals Codex* (19), or the *British Pharmacopeia* (20). Typical specifications are listed in Table 5. Analytical methods required for testing to meet the specifications listed in regulatory texts are described in those texts.

Table 5. Specifications for Benzoic Acid

Propertya	Industrial	Technical	USP FCC[a]
appearance	light tan flakes	white flakes	
odor	characteristic	characteristic	
chlorinated compounds	none	none	
assay[b], %	97.5, min	99.0, min	99.5–100.5
congealing range[c]			121–123°C
residue on ignition, % max			0.05
arsenic (as As), ppm max			3
heavy metals (as Pb), ppm max			10
water, max %			0.7
readily carbonizable substances			passes test
readily oxidizable substances			passes test

[a] Specifications of the USP and FCC are essentially identical.

[b] Anhydrous basis.

[c] Termed "solidification point" in the *Food Chemicals Codex*.

Trace impurities present in commercial benzoic acid include methyl diphenyls and phthalic acids. The concentration and presence of these impurities vary by product grade and by manufacturer. Gas chromatography and high pressure liquid chromatography are useful for determining the concentrations of those impurities.

Industrial and technical grades of benzoic acid are available in molten as well as solid forms (called flakes or chips). USP FCC grade is available in solid form either as crystals or powder. The solid forms of the industrial and technical grade are usually packaged in 50 lb (23 kg) and 25 kg polylined bags and also in "supersacs," each supersac containing from 1000 lb (45.5 kg) to 1000 kg of product. USP FCC grade is usually packaged in polylined fiber drums, each containing 100 lb (45.5 kg), 50 kg, or 200 lb (91 kg).

Molten benzoic acid (industrial or technical) is transported in type 316 stainless steel tank cars, usually 76 m^3 (20,000 gallons) of product, or in ~5,000 gallon (19 m^3) 316 stainless steel tank trucks.

Toxicity, Safety, and Handling

Benzoic acid's toxicity is rated as moderate (3 on a scale of 1–6) based upon its LD_{50} (oral-rat) of 2530 mg kg. Healthy individuals may tolerate small doses (under 0.5 g of benzoates per day) mixed with food without ill effects. Large doses, up to 4 g of sodium benzoate per day, have mainly digestive effects such as gastric pain, nausea, and vomiting. A 67 kg man reportedly ingested single doses of 50 g without ill effects, although the mean lethal dose in dogs and cats is 2.5 g kg (21).

In the early 1900s several food inspection decisions regarding the use of benzoic acid and sodium benzoate were issued, the latter based upon

human feeding studies. As a result of these decisions, since 1909 sodium benzoate and benzoic acid have been allowed to be added to foods at concentrations not to exceed 0.1% (22). A hazard analysis of benzoic acid and a detailed reference on the toxicity of benzoic acid are available (23,24). Manufacturer's product and information bulletins provide an excellent source for information regarding the safety and handling of benzoic acid.

The principal safety concern in handling molten benzoic acid is its elevated temperature. Thermal burns may result from improper handling of the molten product (25,26).

Uses

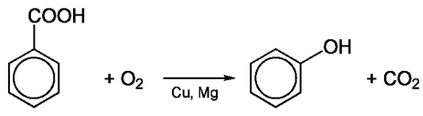
Although the main uses for benzoic acid are as a chemical raw material, it also has numerous direct uses. Benzoic acid is used in substantial quantities to improve the properties of various alkyd resin coating formulations, where it tends to improve gloss, adhesion, hardness, and chemical resistance. Benzoic acid terminates chain propagation in alkyd resins (qv) and promotes crystallinity in the final product.

Benzoic acid is also used as a down-hole drilling mud additive where it functions as a temporary plugging agent in subterranean formations. Since this is a secondary oil recovery application, this use is heavily dependent on the price of crude oil.

In medicine, the internal uses of benzoic acid are relatively unimportant. Its principal medicinal use is external; it is used in dermatology as an antiseptic stimulant and irritant. Combined with salicylic acid *[69-72-7]*, benzoic acid is employed in the treatment of ringworm of the scalp and other skin diseases (Whitfield's ointment).

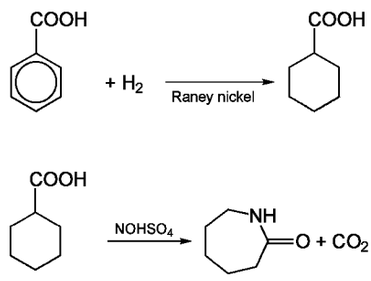
The largest use for benzoic acid is as a chemical raw material in the production of phenol, caprolactam, glycol dibenzoate esters, and sodium and or potassium benzoate.

Phenol. In the early 1960s The Dow Chemical Company built three phenol (qv) plants utilizing benzoic acid as the feedstock (6,27). Dow is no longer involved with these plants, but all three are currently operating and another came on line in Japan in 1991. In this process benzoic acid is air-oxidized to phenol *[108-95-2]* in a liquid-phase reaction utilizing copper and magnesium catalysts according to the following:



The hydroxyl group of the resulting phenol is situated immediately adjacent to where the carboxyl group was previously located. This same liquid-phase copper oxidation process chemistry has been suggested for the production of cresols by the oxidation of toluic acids. *m*-Cresol would be formed by the oxidation of either ortho or para toluic acids; a mixture of *o*- and *p*-cresols would be produced from *m*-toluic acid (6). A process involving the vapor-phase catalytic oxidation of benzoic acid to phenol has been proposed, but no plants have ever been built utilizing this technology (27).

Caprolactam. At the same time that Dow was constructing toluene to phenol plants, Snia Viscosa (28–30) introduced two processes for the manufacture of caprolactam (qv) from benzoic acid. The earlier process produced ammonium sulfate as a by-product, but the latter process did not. In either process benzoic acid is hydrogenated to cyclohexanecarboxylic acid *[98-89-5]*, which then reacts with nitrosylsulfuric acid to form caprolactam *[105-60-2]*.



Glycol Dibenzoates. The benzoate esters of several glycols are another large use for benzoic acid. These high boiling, chemically stable esters find application as plasticizers in the manufacture of floor coverings, vinyl extrusions, plastisols, adhesives, and coatings. The most common types of resins modified with glycol dibenzoates are poly(vinyl acetate) and poly(vinyl chloride). A wide variety of glycol esters have been prepared and evaluated as plasticizers (qv).

Detailed sales and production information has not been published, but it is believed that the bulk of the commercial production consists of the dibenzoate esters of diethylene and dipropylene glycol. These glycol dibenzoates are fast-fusing plasticizers that compete favorably with butyl benzyl phthalate. The properties of these two esters are shown in Table 6 (31). Propylene glycol dibenzoate *[19224-26-1]* and polyethylene glycol 200 dibenzoate also have applications in certain areas. Dipropylene glycol dibenzoate and diethylene glycol dibenzoate both have FDA approval for use in adhesive and food packaging applications (32).

Table 6. Physical Properties of Selected Glycol Dibenzoates

Property	Dipropylene glycol dibenzoate	Diethylene glycol dibenzoate
CAS Registry Number	*[27138-31-4]*	*[120-55-8]*
molecular formula	$C_{20}H_{22}O_5$	$C_{18}H_{18}O_5$
mol wt	342	314
specific gravity, 25°C	1.129	1.178
freezing point, °C	30	28
bp, at 0.7 kPa[a], °C	232	240
refractive index, 25°C	1.5282	1.5424
flash point, tcc, °C	>149	>149
viscosity, 20°C, mPa·s (cP)	170	70

[a] To convert kPa to mm Hg, multiply by 7.5.

Sodium and Potassium Benzoate. These salts are available in grades meeting the specifications of the *National Formulary* (18) and the *Food Chemicals Codex* (19) (Table 7). Sodium benzoate *[532-32-1]* is produced by the neutralization of benzoic acid with caustic soda and or soda ash. The resulting solution is then treated to remove trace impurities as well as color bodies and then dried in steam heated double drum dryers. The product removed from the dryers is light and fluffy and in order to reduce shipping and storage space the sodium benzoate is normally compacted. It is then milled and classified into various product forms, the names of which often bear little relationship to the actual form of the product.

Table 7. Specifications for Sodium and Potassium Benzoate

Property	Sodium benzoate NF FCC[a]	Potassium benzoate food grade[b]
molecular formula	$C_7H_5NaO_2$	$C_7H_5KO_2$
identification	passes tests	passes tests
assay[c], %	99.0–100.5	99.0–100.5
alkalinity (as NaOH), max %	0.04	0.06
arsenic (as As), ppm max	3	3
heavy metals (as Pb), ppm max	10	10
water, max %	1.5	1.5

[a] Specifications of the *National Formulary* and the *Food Chemicals Codex* are identical.

[b] Potassium benzoate will be included in the *Food Chemical Codex* in the next supplement. Until such time potassium benzoate is sold as food-grade.

[c] Anhydrous basis.

Potassium benzoate *[582-25-2]* is produced by neutralizing benzoic acid with caustic potash. The resulting solution is processed in a fashion nearly identical to that of sodium benzoate. Product forms are also similar.

Sodium and potassium benzoate are employed in a wide range of preservative applications because they provide an effective combination of antimicrobial action, low cost, and safety. Although sodium and potassium benzoate are the preservatives offered in the marketplace, the actual active ingredient being sold is free (or undissociated) benzoic acid. The benzoate ion has essentially no antimicrobial properties. Since it is the undissociated (free) benzoic acid that provides the antimicrobial action, sodium benzoate and potassium benzoate are recommended for use in application areas where the pH is at 4.5 or lower (Table 8).

Table 8. Undissociated (Free) Benzoic Acid vs pH

pH	Free benzoic acid, %	pH	Free benzoic acid, %
3	93.5	6	5.1
4	59.3	7	0.5
5	12.8		

Benzoic acid is supplied to this market in the form of salts because the benzoate salts have a high solubility in water and aqueous stock solutions of up to 35% can easily be prepared. In addition, it is easier, and therefore cheaper, to purify sodium and potassium benzoate than to produce the USP FCC grade of benzoic acid.

Sodium and potassium benzoate are substances that may be added directly to human food and are affirmed as GRAS (33–35). Benzoic acid and sodium and potassium benzoate are now used as preservatives in such foods as sauces, pickles, cider, fruit juices, wine coolers, syrups and concentrates, mincemeat and other acidic pie fillings, margarine, egg powder, fish (as a brine dip component), bottled carbonated beverages, and fruit preserves, jams, and jellies. The popularity of diet soft drinks has led to increased demand for both benzoate salts.

Nonfood preservative applications of sodium and potassium benzoate are found in pharmaceutical and cosmetic preparations, such as toothpastes and powders, tobacco, pastes and glue, as well as starch and latex (36,37).

The use of the potassium salt of benzoic acid is relatively new. Concerns regarding sodium intake and its possible relationship to high blood pressure have caused some soft drink manufacturers to switch to potassium benzoate.

Sodium benzoate is also finding increasing application as a corrosion inhibitor. It is incorporated into paper wrapping materials for the prevention of rust or corrosion in the production of such diverse items as razor blades, engine parts, bearings, etc. It is also used in the automotive industry as a corrosion inhibitor in engine cooling systems (at ~1.5%), mainly in Europe and Japan. Unlike in its application as a preservative where free benzoic acid is required to provide antimicrobial action, it appears to be the benzoate ion that provides the corrosion protection.

Benzoic Acid Derivatives

Benzoyl chloride, *[98-88-4]*, C_6H_5COCl, mp, −1°C; bp, 197.2°C at 101.3 kPa; d_4^{26}, 1.2070; n_D^{20}, 1.55369. Benzoyl chloride is a colorless liquid that fumes upon exposure to the atmosphere, has a sharp odor, and in vapor form is a strong lachrimator. It is decomposed by water and alcohol, and is miscible with ether, benzene, carbon disulfide, and oils. Benzoyl chloride may be prepared in several ways, including the partial hydrolysis of benzotrichloride, the chlorination of benzaldehyde, and from benzoic acid and phosphorus pentachloride. The most common method is the reaction of benzoic acid and benzotrichloride *[98-07-7]*. Since benzoic acid may be easily obtained from benzotrichloride, the latter is used as the sole raw material for large-scale production of benzoyl chloride.

Benzoyl chloride is an important benzoylating agent. In this use the benzoyl radical is introduced into alcohols, phenols, amines, and other compounds through the Friedel-Crafts reaction and the Schotten-Baumann reaction. Other significant uses are in the production of benzoyl peroxide *[94-36-0]*, benzophenone *[119-61-9]*, and in derivatives employed in the fields of dyes, resins, perfumes, pharmaceuticals, and as polymerization catalysts.

Benzoic anhydride, *[93-97-0]* $(C_6H_5CO)_2O$, mp, 42°C; bp, 360°C at 101.3 kPa; d_4^{16}, 1.1989; n_D^{15}, 1.157665. Almost insoluble in water, benzoic anhydride is soluble in most common solvents. A number of methods for the preparation of benzoic anhydride are reported (38). Probably the best is the reaction of benzoyl chloride and benzoic acid (39).

$$C_6H_5COOH + C_6H_5COCl \rightarrow (C_6H_5CO)_2O + HCl$$

Benzoic anhydride is not manufactured on a large scale. Its primary use is as a benzoylating agent in the manufacture of pharmaceuticals and chemical intermediates.

BENZOIC ACID SALTS

Ammonium benzoate [1863-63-41], $C_6H_5COONH_4$, mp, 198°C. This is a dull white powder which gradually loses ammonia on exposure to air. Its aqueous solution, it is slightly acidic. Ammonium benzoate has been suggested as a component in certain rubber formulations (40) and as a preservative in paints and glues.

Sodium benzoate [532-32-1], C_6H_5COONa, is highly soluble in water (61.2 g dissolve in 100 g of water at 25°C) and somewhat soluble in ethyl alcohol, glycerol, and methanol. A 25% aqueous solution of sodium benzoate exhibits a pH of 7.5–8.

Potassium benzoate [582-25-2], C_6H_5COOK, is even more soluble in water than sodium benzoate (73.6 g dissolve in 100 g of water at 25°C). A 25% aqueous solution of potassium benzoate exhibits a pH of 8–8.5.

BENZOIC ACID ESTERS

Benzyl benzoate, *[120-51-4]*, $C_6H_5COOCH_2C_6H_5$, mp, 21°C, d_4^{25}, 1.118; bp, 323–324°C at 101.3 kPa; n_D^{21}, 1.5681. This is a colorless, oily liquid with a faint, pleasant aromatic odor and a sharp, burning taste. It occurs naturally in Peru and Tolu balsams, is sparingly volatile with steam, and is insoluble in water. Benzyl benzoate is prepared commercially by the direct esterification of benzoic acid and benzyl alcohol or by reaction of benzyl chloride and sodium benzoate. The pleasant odor of benzyl benzoate, like other benzoic esters, has long been utilized in the perfume industry, where it is employed as a solvent for synthetic musks and as a fixative. It has also been used in confectionery and chewing gum flavors.

Benzyl benzoate has been used as an insect repellent in formulations for repelling mosquitoes, chiggers, ticks, and fleas, and in the control of livestock insects. Benzyl benzoate was used in the Vietnam War to eradicate and repel certain ticks and mites. It has also found some usage in medicine, cosmetics, and as a plasticizer.

Butyl benzoate, *[136-60-7]*, $C_6H_5COOC_4H_9$, mp, 22°C; bp, 250°C at atm 101.3 kPa. This ester is a thick, oily liquid that has found usage as a dye carrier for polyester fibers.

Ethyl benzoate, *[93-89-0]*, $C_6H_5COOC_2H_5$, mp, 35°C; bp, 212°C at 101.3 kPa; d_4^{20}, 0.8788. Used in synthetic ylang-ylang oil, ethyl benzoate is similar in odor to methyl benzoate but is reportedly smoother.

n-Hexyl benzoate, *[6789-88-4]*, $C_6H_5COOC_6H_{13}$, bp, 272°C at 103.9 kPa. This is used in perfumery as a fixitive and has a melonlike odor.

Methyl benzoate, *[93-58-3]*, $C_6H_5COOCH_3$, bp, 198–200°C at 101.3 kPa; d_4^{15}, 1.094; n_D^{15}, 1.5205. Insoluble in water, this is a colorless, transparent liquid solidifying at about 15°C. Methyl benzoate is prepared by the direct esterification of benzoic acid and methanol. It is used in the fragrance industry and in the production of other benzoate esters (via transesterification). A technical-grade methyl benzoate is available as a by-product in the manufacture of dimethyl terephthalate *[120-61-6]*.

Phenyl benzoate, *[93-99-2]*, $C_6H_5COOC_6H_5$, mp, 70–71°C; bp, 314°C at 101.3 kPa. This has been suggested as an antioxidant (qv) for certain high temperature lubricants (41). Phenyl benzoate exists as a nonisolated intermediate in the production of phenol from benzoic acid.

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BENZOIN.

See BENZALDEHYDE; RESINS, NATURAL.

BENZOL.

See BENZENE.

BENZOPHENONE.

See KETONES.

BENZOQUINONE.

See QUINONES.

BENZOTRICHLORIDE.

See CHLOROCARBONS AND CHLOROHYDROCARBONS—BENZYL CHLORIDE, BENZAL CHLORIDE, BENZOTRICHLORIDE.

BENZOYL CHLORIDE.

See BENZOIC ACID.

BENZOYL PEROXIDE.

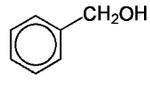
See PEROXIDES AND PEROXY COMPOUNDS, ORGANIC.

BENZYL ACETATE.

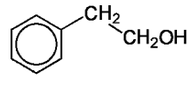
See ESTERS, ORGANIC.

BENZYL ALCOHOL AND β-PHENETHYL ALCOHOL

Benzyl alcohol (1) and β-phenethyl alcohol (2) (2-phenylethanol) are the simplest of the aromatic alcohols, and, as such, are chemically similar. Their physical properties are given in Table 1.



(1)



(2)

Table 1. Physical Properties of Benzyl Alcohol and β-Phenethyl Alcohol

Property	Benzyl alcohol	β-Phenethyl alcohol

molecular formula	C_7H_8O	$C_8H_{10}O$
CAS Registry Number	*[100-51-6]*	*[60-12-8]*
mp, °C	−15	25.8
bp at 101.3 kPa[a], °C	205.4–205.7	219.5–220
bp at 1.33 kPa[a], °C	89.0–89.5	99–100
d_{15}^{15}		1.0242
d_{25}^{25}	1.0441	1.017
n_D^{20}	1.53955	1.5323
flash point, closed cup, °C	100.4	
open cup, °C	104.4	
autoignition temp, °C	436	
vapor density (air = 1)	3.7	
vapor pressure at 58°C, kPa[a]	0.133	0.133
100°C, kPa[a]	2.02	1.33
surface tension at 20°C, mN/m (=dyn/cm)	39	
80°C, mN/m (=dyn/cm)	33	
viscosity at 25°C, mPa·s(=cP)	5.05	7.58
50°C, mPa·s(=cP)		3.19
solubility at 25°C, water	1 g/25 mL	1 g/51 mL
30% ethanol		1 g/12 mL
50% ethanol	1 g/1.5 mL	1 g/1.7 mL

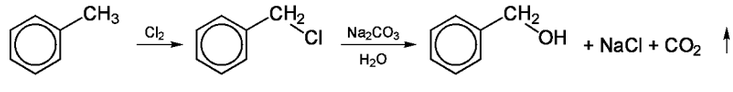
[a] To convert kPa to mm Hg, multiply by 7.5.

Benzyl Alcohol

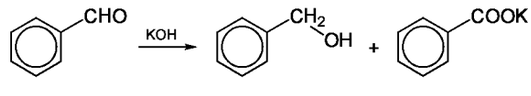
Benzyl alcohol (1) occurs widely in essential oils both as the free alcohol, and, more importantly from a fragrance standpoint, in the form of various esters. Although benzyl alcohol itself is rather bland in odor, combined with its much more fragrant esters it is an important part of the odor of jasmine, ylang-ylang, gardenia, some rose varieties, narcissus and peony, as well as castoreum, balsams of peru and tolu, and propolis. Benzyl alcohol occurs primarily in flower oils and tree exudates, whereas a large number of essential oils obtained from other parts of a wide variety of plants contain no benzyl alcohol or its esters (1).

Benzyl alcohol readily undergoes the reactions characteristic of a primary alcohol, such as esterification and etherification, as well as halide formation. In addition, it undergoes ring substitution. In the presence of acid, polymerization is observed, and the alcohol can be thermally dehydrated to toluene *[108-88-3]*. Catalytic oxidation over copper oxide yields benzaldehyde; benzoic acid is obtained by oxidation with chromic acid or potassium permanganate. Catalytic hydrogenation of the ring gives cyclohexylmethanol *[100-49-2]*.

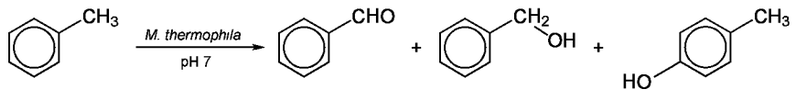
Manufacture. Today benzyl alcohol is almost universally manufactured from toluene which is first chlorinated to give benzyl chloride *[100-44-7]*. This is then hydrolyzed to benzyl alcohol by treatment with aqueous sodium carbonate.



Prior to the commercial development of this process benzyl alcohol was obtained from benzaldehyde *[100-52-7]* which undergoes the Cannizzaro reaction (2) upon treatment with potassium hydroxide. High yields of benzyl alcohol and potassium benzoate are obtained by this route which cannot compete with the present day process because of the high cost of benzaldehyde (qv).



In the future it may be possible to oxidize toluene microbially to produce benzyl alcohol. Treatment of toluene in the presence of air with a culture of *M. thermophila* in a phosphate buffer is reported to yield a mixture of benzaldehyde, benzyl alcohol, and *p*-cresol *[106-44-5]* (3).



World Consumption and Uses. Eleven companies in the United States, Western Europe, and Japan have a total annual capacity for benzyl chloride of over 154,000 t. In 1988, total production for these three regions was 97,000 t. Overall, 1988 consumption exceeded 91,000 t, of which benzyl alcohol accounted for 23% or approximately 21,000 t (4).

In the soap, perfume, and flavor industries benzyl alcohol is primarily used in the form of its aliphatic esters. Benzyl benzoate *[120-51-4]* finds widespread use as a fragrance diluent. Benzyl alcohol is frequently employed in bar soap fragrances at 30–40 wt % of the fragrance. Benzyl alcohol is commercially available in five grades (Table 2).

Table 2. Specifications of Benzyl Alcohol[a]

	Grade				
Determination	Technical	NF	Reagent	Photo[b]	Textile
assay (OH determination)	98% min	99% min	99.0% min	99% min	99% min
solubility in water at 25°C	1 g/30 mL	1 g/30 mL	1 g/25 mL	1 g/25 mL	1 g/25 mL (at 50°C)
benzaldehyde content (uv determination)	0.3% max	0.2% max	0.03% max	0.04% max	0.2% max
halogen (Beilstein)	0.1% max	neg	neg	neg	neg

[a] Benzyl alcohol is sold in fractional and 3.5-kg glass bottles, and steel drums containing 22, 113, and 208 kg. The photo and textile grades are available in tankwagon and tankcar quantities. Freight classification: chemicals, NOIBN; ICC regulations, none.

[b] Photo grade contains 0.01–0.02% of a hydroquinone monomethyl or benzyl ether to prevent the oxidation of the alcohol to benzaldehyde.

The largest proportion of benzyl alcohol is for use in the photographic and textile industries although the latter use has been declining. The photo grade is used in a developing bath for color motion pictures (5), for the development of color transparencies (6), as a dispersing reagent for silver halide grains in mixed packet emulsions (7), as a stop bath for production of lithographic plates (8–10), as a dispersing agent and film softener in an antistatic treating compound (11), and as an activator in a print-out image method (12). The textile grade is used as a dyeing assistant for wool (13–15) and nylon (16).

The NF and reagent grades are employed in the pharmaceutical industry which makes use of benzyl alcohol's local anesthetic, antiseptic, and solvent properties (17–20). It also finds use in cough syrups and drops; ophthalmic solutions; burn, dental (21), and insect repellant solutions and ointments; and dermatological aerosol sprays. It is used in nail lacquers and as a color developer in hair dyes by the cosmetics industry (22), and in acne treatment preparations (23).

Because of its strong polarity and limited water solubility, the technical grade of benzyl alcohol is used in rug cleaners as a degreasing agent (24), in leather dyeing (25), in ballpoint inks (26), as a cleaner for soldering (27), and as an extractive distillation solvent for xylenes and cresols (28,29). It is used as a stabilizer in insecticidal formulations by the agriculture industry (30) and in treating fruits and vegetables (31). In addition, benzyl alcohol is used extensively in the polymer industry (32–37) and in the manufacture of automobile tires (38).

Health and Safety. Benzyl alcohol is listed on the U.S. *Toxic Substances Control Act* (TSCA) *Chemical Substances Inventory*, the *European Inventory of Existing Commercial Chemical Substances* (EINECS), *Australian Cone Inventory of Chemical Substances*, and the *Canadian Domestic Substances List* (DSL) (39–42). This material has a Generally Recognized As Safe (GRAS) status indicated by the Flavor and Extract Manufacturers' Association for use in flavors and by the Council of Europe for use as a flavor (43–45). Benzyl alcohol satisfies the most current guidelines published by the International Fragrance Association (IFRA) which governs the use of fragrance materials (46).

Human sensitization studies were negative at 10% solution (47). Undiluted benzyl alcohol produces moderate dermal irritation in guinea pigs and mild dermal irritation in rabbits (48,49). Severe eye irritation was noted in a rabbit study (50). Acute oral rat LD_{50} values were reported between 1.23 and 3.10 g kg (50–52). A dermal rabbit LD_{50} value of 2.0 g kg has been reported (49). Rats died after 2 h when exposed to a 200-ppm vapor concentration (53). Benzyl alcohol is readily oxidized in animals and humans to benzoic acid *[65-85-0]* which is then conjugated with glycine *[56-40-6]*, and rapidly eliminated in the urine as hippuric acid *[495-69-2]* (54).

National Toxicology Program (NTP) carcinogenicity studies in rats and mice were negative and benzyl alcohol was not mutagenic when tested in the NTP Genetic Toxicology Program (49,55).

β-Phenethyl Alcohol

Of all the aromatic organic molecules β-phenethyl alcohol (PEA) (2) is probably the most prestigious aroma chemical in the world of perfumery. This is because of its exquisite odor of natural rose petals.

Twenty-four years before its detection in nature PEA was first synthesized in 1876 (56) by reducing phenylacetaldehyde *[122-78-1]* with sodium amalgam. Then, in 1900, it was independently identified in otto of rose (57) and rose water (58). Subsequently, PEA has been identified in numerous flower oils such as ylang-ylang, narcissus, hyacinth, lily, neroli, and geranium as well as various other natural products like tea, tobacco, orange juice, beer, cigarette smoke, etc.

Physical properties of PEA are shown in Table 1. The pure compound is extremely difficult to crystallize because it tends to supercool to a glass. In addition, it forms a number of azeotropes (59).

The compound undergoes the usual chemical reactions of alcohols or aromatic compounds. The hydroxyl group can be replaced by halogens and can be readily esterified with practically any organic acid in the presence of sulfuric acid as a catalyst. It combines with anhydrous calcium chloride to give a solid addition compound formerly used in purifying the alcohol. It forms acetals with many aldehydes. Phenethyl alcohol dehydrates in the presence of acids to bis(phenethyl)ether *[93-96-9]*, whereas with alkali, it gives styrene. With other alcohols, it forms mixed ethers. Dehydrogenation to phenylacetaldehyde can be effected with finely divided metallic catalysts, such as copper and silver or zinc oxide in the presence of oxygen. Oxidation with dichromate or permanganate yields phenylacetic acid *[103-82-2]*, and finally benzoic acid. With nitric oxide the primary product of oxidation is phenylacetic acid with similar amounts of phenylacetaldehyde (60). Since it contains an aromatic ring, PEA can be nitrated, sulfonated, and chlorinated; it can be hydrogenated to 2-cyclohexylethanol *[4442-79-9]* (61–64), which is not only a natural product (65,66), but also a perfume chemical. It has also been found in fresh tearose leaves (67).

In insect control, PEA has been considered as a mosquito repellant (68), and its acetate has been used as an ingredient in Japanese beetle bait (69). The alcohol also has bacteriostatic action and antifungicidal properties (70–73), and it has been claimed as a surface-active agent (74).

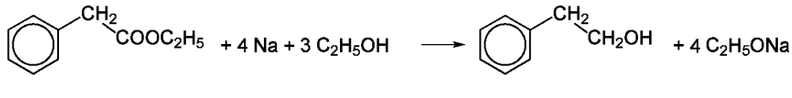
Phenethyl alcohol may be identified as the phenethyl *p*-nitrobenzoate *[57455-00-2]* (mp 106–108°C), as phenethyl *p*-nitrobenzyl phthalate *[65997-34-4]* (mp 84.3°C), and also by its formation of styrene on treatment with alkali. Use of these derivatives has, however, been superseded by physical methods. Infrared (75,76), mass spectroscopy (77), and nmr spectra (78) are useful for identification.

Pure PEA possesses an extremely mild roselike odor. Commercial grades of PEA which are >99% pure vary in odor because of the impurities present which depend on the method of manufacture. The common impurities are benzaldehyde *[100-52-7]*, benzylacetone *[2550-26-7]*, 1-phenyl-2-propanol *[14898-87-4]*, and phenylacetaldehyde. It is claimed that the presence of phenylacetaldehyde imparts a honeylike by-odor resembling the odor of dried rose leaves with a faint suggestion of otto of rose which has a honey by-note. However, the presence of phenylacetaldehyde above 0.01% greatly distorts the delicate rose odor of PEA.

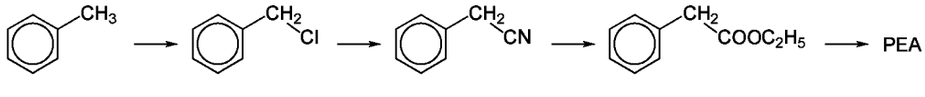
Because of factors of low cost, stability, and odor quality, PEA is ideally suited for use in bar soap fragrances where its use can be up to 30–50% of the fragrance.

Manufacture. Commercial methods for making PEA can be broadly divided into three categories: historical, present, and future methods.

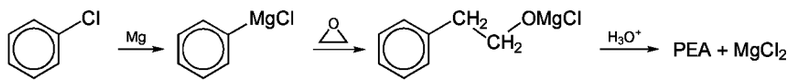
Methods Primarily of Historical Interest. In the *Bouveault-Blanc Reduction* (79,80) phenylacetic ester is reduced with sodium and alcohol to PEA.



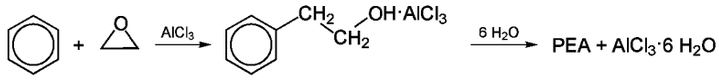
In *Leonard's Method* (81) toluene is chlorinated to benzyl chloride which is, in turn, converted to phenylacetic ester, and then to PEA.



Present Day Methods. In the *Grignard Synthesis* (82,83), chlorobenzene *[108-90-7]* is converted to phenylmagnesium chloride which reacts with ethylene oxide *[75-21-8]* at 100°C to give β-phenylethoxy magnesium chloride which is then decomposed with sulfuric acid to give PEA.

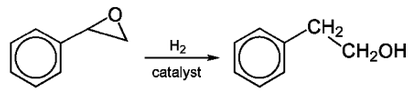


The *Friedel-Crafts* process (84,85) produces most of the PEA presently being manufactured.

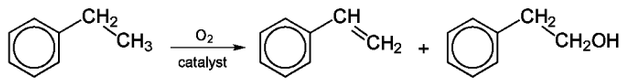


Because PEA is such an important fragrance material this simple, essentially one-step process has been exhaustively studied to optimize reaction conditions and purification procedures. Because of the high reactivity of the intermediates and the tendency toward polymer formation, critical factors such as throughput, temperature, molar ratios of reactants, addition rates, reactor materials and design, and agitation rate must be carefully balanced to provide an economical product with acceptable odor properties.

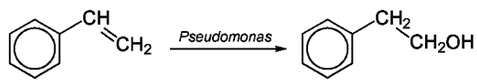
Catalytic hydrogenation of styrene oxide (86–99) is another process currently used for the manufacture of PEA. The main requirements for this reaction are a low operating temperature to avoid side reactions and a good quality of styrene oxide *[76-09-3]* starting material.



Future Methods. A by-product stream containing 60–80% PEA can be obtained from the catalytic air oxidation of ethylbenzene *[100-41-4]* (100). Perfumery-grade material can be isolated from this stream by complexing the PEA with a metal halide (such as $CaCl_2$), separation of the adduct, and thermal decomposition followed by distillation.



Microbiological Oxidation. Styrene *[100-42-5]* can be oxidized to PEA by aerobic culturing with a *Pseudomonas* bacterium in the appropriate medium (101). For a medium containing peptone, $(NH_4)_2SO_4$, $Na_2HPO_4 \cdot 12H_2O$, KH_2PO_4, $MgSO_4$, and corn steep liquor, the yield is 2.34 mg mL.



Purification. Purification problems are primarily solved by two methods: continuous vacuum fractionation and chemical combination to yield a high boiling ester, separation of the noncombining impurities by distillation, and hydrolysis of the ester. Although the product produced by continuous vacuum fractionation satisfies most needs, shows no impurities by glc, is odor-acceptable, and thus is used to produce most of the PEA for commercial use, for highest requirements chemical purification by the borate ester is required.

World Consumption. The estimated total world consumption of PEA and its esters for 1990 was 7000 t. Of this figure, one-fourth was used in North America and 43% in East and West Europe. Approximately 85% of the PEA is employed for fragrance use (102).

Health and Safety. The use of β-phenethyl alcohol generally presents no health problems. PEA is listed on the U.S. (TSCA), (EINECS), *Australian Care Inventory of Chemical Substances*, and the Canadian (DSL) (39–42). This material has Generally Recognized As Safe (GRAS) status as indicated by the Flavor and Extract Manufacturers Association and is approved by the U.S. Food and Drug Administration and the Council of Europe for use in flavors (43–45). PEA satisfies the most current guidelines published by the International Fragrance Association (IFRA) which governs the use of fragrance materials (46).

PEA was negative when tested at 8% in human dermal sensitization and irritation studies (103). Undiluted material caused slight to moderate irritation when applied to guinea pig skin (48,49), and moderate irritation on rabbit skin (48,49); it was severely irritating to the rabbit eye (50). Oral rat LD_{50} values of 1.5, 1.79, and 2.46 g kg have been reported (47,48,104). Mouse LD_{50} values of 0.8–1.5 g kg and a dermal rabbit LD_{50} of 0.79 g kg have been recorded (49). An 8-h exposure to a saturated vapor atmosphere caused no mortality in rats (50). No significant effects other than decreased weight gain at high doses were observed after a 90-d dermal study in rats (105). Maternally nontoxic dermal doses of PEA caused no adverse fetal effects in rats (106).

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BENZYLAMINE.

See QUINOLINE AND ISOQUINOLINES.

BENZYL CHLORIDE.

See CHLOROCARBONS AND CHLOROHYDROCARBONS—BENZYL CHLORIDE, BENZAL CHLORIDE, BENZOTRICHLORIDE.

BERKELIUM.

See ACTINIDES AND TRANSACTINIDES.

BERYLLIDES.

See BERYLLIUM AND BERYLLIUM ALLOYS.

BERYLLIUM AND BERYLLIUM ALLOYS

Beryllium *[7440-41-7]*, Be, specific gravity — 1.848 g mL, and mp of 1287°C, is the only light metal having a high melting point. The majority of the beryllium commercially produced is used in alloys, principally copper–beryllium alloys (see COPPER ALLOYS). The usage of unalloyed beryllium is based on its nuclear and thermal properties, and its uniquely high specific stiffness, ie, elastic modulus density values. Beryllium oxide ceramics (qv) are important because of the very high thermal conductivity of the oxide while also serving as an electrical insulator. The only commercial extraction plant operating in the Western world is that of Brush Wellman at Delta, Utah using both beryl and bertrandite ores as input.

Occurrence The beryllium content of the earth's surface rocks has been estimated at 4–6 ppm (1). Although ca 45 beryllium-containing minerals have been identified, only beryl *[1302-52-9]* and bertrandite *[12161-82-9]* are of commercial significance.

Gemstone beryl (emerald, aquamarine, and beryl) approaches a pure beryllium–aluminum–silicate composition, $3BeO \cdot Al_2O_3 \cdot 6SiO_2$. Beryl is widely distributed in fine-grained, unzoned pegmatite dikes and in pockets in zoned pegmatite dikes. Beryl is usually obtained as a by-product from mining zoned pegmatite deposits to recover feldspar *[68476-25-5]*, spodumene *[1302-37-0]*, or mica *[12001-26-2]*. The crushed ore is hand sorted to yield the characteristically hexagonal-shaped beryl crystals that are frequently green or blue in color. Beryl is primarily obtained from Brazil but commercial deposits also occur in China, Argentina, Africa, India, and Russia. A BeO content of 10% is considered necessary for the economic extraction of beryllium from beryl ore.

Bertrandite, $4BeO \cdot 2SiO_2 \cdot H_2O$, became of importance in 1969 when the deposits of Spor Mountain in the Topaz district of Utah were commercially opened. These deposits are believed to have been derived from fluorine-rich hydrothermal solutions at shallow depths (2). Whereas economical beneficiation of these ores averaging <1% BeO has not been achieved, these deposits are commercially viable because of the large reserves present, open-pit mining, and the fact that the beryllium may be extracted by leaching with sulfuric acid. Although some beryl is processed, the majority of beryllium is now obtained from bertrandite.

Properties

A summary of physical and chemical constants for beryllium is compiled in Table 1 (3–7). One of the more important characteristics of beryllium is its pronounced anisotropy resulting from the close-packed hexagonal crystal structure. This factor must be considered for any property that is known or suspected to be structure sensitive. As an example, the thermal expansion coefficient at 273 K of single-crystal beryllium was measured (8) as 10.6×10^{-6} parallel to the *a*-axis and 7.7×10^{-6} parallel to the *c*-axis. The actual expansion of polycrystalline metal then becomes a function of the degree of preferred orientation present and the direction of measurement in wrought beryllium.

Table 1. Physical and Chemical Properties of Beryllium

Parameter	Value
at no.	4
at wt	9.0122
electronic structure	$1s^2 2s^2$
at radius, pm	112.50
at vol at 298 K, mL mol	4.877
crystal lattice constants, pm	
α-Be, hexagonal close-packed (HCP)	a = 228.56, c = 358.32, c/a = 1.5677
β-Be, body-centered cubic (BCC) at 1523 K	a = 255.0
transformation pt, HCP to BCC, K	1527
mp, °C	1287
bp, °C	2472
density, g mL	

at 298 K	1.8477
at 1773 K	1.42
heat of fusion, ΔH_{fus}, J g[a]	1357
heat of sublimation, ΔH_s, kJ g[a]	35.5–36.6
heat of vaporization, ΔH_v, kJ g[a]	25.5–34.4
heat of transformation, J g[a]	837
standard entropy, $S°$, J (g·K)[a]	1.054
standard enthalpy, $H°$, J g[a]	216
contraction on solidification, %	3
vapor pressure, MPa[b]	
at 500 K	5.7×10^{29}
at 1000 K	4.73×10^{12}
at 1560 K	4.84×10^{6}
specific heat, J (g·K)[a]	
at 298 K	1.830
at 700 K	2.740
thermal conductivity at 298 K, W (m·K)	220
linear coefficient of thermal expansion, 278–333 K[c]	11.4×10^{6}
electrical resistivity at 298 K, Ω·m	4.31×10^{8}
reflectivity, %	
white light	50–55
infrared (10.6 μm)	98
sound velocity, m s	12,600

[a] To convert J to cal, divide by 4.184.

[b] To convert MPa to psi, multiply by 145.

[c] Value is for unworked, isostatically pressed powder metallurgy metal.

Beryllium has a high x-ray permeability approximately seventeen times greater than that of aluminum. Natural beryllium contains 100% of the ^{9}Be isotope. The principal isotopes and respective half-life are Be, 0.4 s; ^{7}Be, 53 d; ^{8}Be, 10^{16} s; ^{9}Be, stable; ^{10}Be, 2.5×10^{6} yr. Beryllium can serve as a neutron source through either the (α,*n*) or (*n,2n*) reactions. Beryllium has a low (9×10^{30} m^2) absorption cross-section and a high (6×10^{28} m^2) scatter cross-section for thermal neutrons making it useful as a moderator and reflector in nuclear reactors (qv). Such application has been limited, however, because of gas-producing reactions and the reactivity of beryllium toward high temperature water.

At ambient temperatures beryllium is quite resistant to oxidation; highly polished surfaces retain the brilliance for years. At 700°C oxidation becomes noticeable in the form of interference films, but is slow enough to permit the working of bare beryllium in air at 780°C. Above 850°C oxidation is rapid to a loosely adherent white oxide. The oxidation rate at 700°C is parabolic but may become linear at this temperature after 24–48 hours of exposure. In the presence of moisture this breakaway oxidation occurs more rapidly and more extensively. Beryllium oxide *[1304-56-9]*, BeO, forms rather than beryllium nitride *[1304-54-7]*, Be_3N_2, but in the absence of oxygen, nitrogen attacks beryllium above 900°C.

Beryllium is susceptible to corrosion under aqueous conditions especially when exposed to solutions containing the chloride ion. It is rapidly attacked by seawater. High purity water, containing small amounts of HNO_3 to passivate stainless steel in the system, was quite inert to beryllium over a period of years in a primary U.S. nuclear test reactor. At high temperatures beryllium reduces water, releasing hydrogen and forming BeO. Owing to its position in the EMF series, beryllium undergoes galvanic corrosion when coupled in a corrosive environment to the common structural metals; manganese, zinc, and magnesium are the only such metals anodic to beryllium. Protective systems used for beryllium include chromic acid passivation, chromate conversion coatings, chromic acid anodizing, electroless plating (qv), and paints.

Beryllium reacts readily with sulfuric, hydrochloric, and hydrofluoric acids. Dilute nitric acid attacks the metal slowly, whereas concentrated nitric acid has little effect. Hot concentrated alkalies give hydrogen and the amphoteric beryllium hydroxide *[13327-32-7]*, $Be(OH)_2$. Unlike the aluminates, the beryllates are hydrolyzed at the boil.

Beryllium reacts with fused alkali halides releasing the alkali metal until an equilibrium is established. It does not react with fused halides of the alkaline-earth metals to release the alkaline-earth metal. Water-insoluble fluoroberyllates, however, are formed in a fused-salt system whenever barium or calcium fluoride is present. Beryllium reduces halides of aluminum and heavier elements. Alkaline-earth metals can be used effectively to reduce beryllium from its halides, but the use of alkaline-earths other than magnesium *[7439-95-4]* is economically unattractive because of the formation of water-insoluble fluoroberyllates. Formation of these fluorides precludes efficient recovery of the unreduced beryllium from the reaction products in subsequent processing operations.

Chemically, beryllium is closely related to aluminum *[7429-90-5]* from which complete separation is difficult.

Ore Processing

Sulfate Extraction of Beryl. The Kjellgren-Sawyer sulfate process (9) is used commercially for the extraction of beryl. The ore is melted at 1650°C and quenched by pouring into water. The resulting noncrystalline glass is heat-treated at 900–950°C to further increase the reactivity of the beryllium component. After grinding to less than 74 μm (200 mesh), a slurry of the powder in concentrated sulfuric acid *[7664-93-9]* is heated to 250–300°C converting the beryllium and aluminum to soluble sulfates. The silica fraction remains in the dehydrated, water-insoluble form. The nearly dry mass is leached with water using a countercurrent decantation washing procedure and the resulting solution is fed to the same type of solvent extraction process as that used for bertrandite extraction.

Extraction of Bertrandite. Bertrandite-containing tuff from the Spor Mountain deposits is wet milled to provide a thixotropic, pumpable slurry of below 840 μm (20 mesh) particles. This slurry is leached with sulfuric acid at temperatures near the boiling point. The resulting beryllium sulfate *[13510-49-1]* solution is separated from unreacted solids by countercurrent decantation thickener operations. The solution contains 0.4–0.7 g L Be, 4.7 g L Al, 3–5 g L Mg, and 1.5 g L Fe, plus minor impurities including uranium *[7440-61-1]*, rare earths, zirconium *[7440-67-7]*, titanium *[7440-32-6]*, and zinc *[7440-66-6]*. Water conservation practices are essential in semiarid Utah, so the wash water introduced in the countercurrent decantation separation of beryllium solutions from solids is utilized in the wet milling operation.

A beryllium concentrate is produced from the leach solution by the counter-current solvent extraction process (10). Kerosene *[8008-20-6]* containing di(2-ethylhexyl)phosphate *[298-07-7]* is the water-immiscible beryllium extractant. The slow extraction of beryllium at room temperature is accelerated by warming. The raffinate from the solvent extraction contains most of the aluminum and all of the magnesium contained in the leach solution.

The loaded organic phase is stripped of beryllium using an aqueous ammonium carbonate *[506-87-6]* solution, apparently as a highly soluble ammonium beryllium carbonate *[65997-36-6]* complex, $(NH_4)_4Be(CO_3)_3$. All of the iron *[7439-89-6]* contained in the leach solution is coextracted with the beryllium. Heating the strip solution to about 70°C separates the iron and a small amount of coextracted aluminum as hydroxide or basic carbonate

precipitates, which are removed by filtration. The stripped organic phase is treated with sulfuric acid to recover the di(2-ethylhexyl)phosphate.

Heating the ammonium beryllium carbonate solution to 95°C causes nearly quantitative precipitation of beryllium basic carbonate [66104-24-3], $Be(OH)_2 \cdot 2BeCO_3$. Evolved carbon dioxide and ammonia are recovered for recycle as the strip solution. Continued heating of the beryllium basic carbonate slurry to 165°C liberates the remaining carbon dioxide and the resulting beryllium hydroxide *[13327-32-7]* intermediate is recovered by filtration. The hydroxide is the basic raw material for processing into beryllium metal, copper–beryllium and other alloys, and beryllia *[1304-56-9]* for ceramic products. Approximately 90% of the beryllium content of bertrandite is recovered by this process.

Production of Beryllium Metal

Reduction of Beryllium Fluoride with Magnesium. The Schwenzfeier process (11) is used to prepare a purified, anhydrous beryllium fluoride *[7787-49-7]*, BeF_2, for reduction to the metal. Beryllium hydroxide is dissolved in ammonium bifluoride solution to give a concentration of 20 g L Be at pH 5.5. The solution is made basic by the addition of solid calcium carbonate and heating to 80°C precipitating residual aluminum. Lead dioxide is added to the solution to convert manganese *[7439-96-5]* to insoluble MnO_2 and to precipitate chromium *[7440-47-3]* as insoluble lead chromate. After filtration, ammonium sulfide is added to the filtrate to remove heavy-metal impurities from the hydroxide and any solubilized lead from the lead dioxide treatment. After filtration and balancing to the proper stoichiometry, ammonium fluoroberyllate *[14874-86-3]*, $(NH_4)_2BeF_4$, is crystallized by concurrent evaporation under vacuum. The salt is continuously removed by centrifugation and washed lightly, the mother liquor and washings being returned to the evaporator. The $(NH_4)_2BeF_4$ is charged into inductively heated, graphite-lined furnaces where it is thermally decomposed to beryllium fluoride and ammonium fluoride. The ammonium fluoride is vaporized into fume collectors for recycle to the dissolving process. The molten beryllium fluoride flows continuously from the bottom of the furnace and is solidified as a glassy product on water-cooled casting wheels (12).

The reduction of beryllium fluoride using magnesium

$$BeF_2 + Mg \rightarrow Be + MgF_2$$

has not been forced above an 85% yield. Complications include: volatilization of unreacted magnesium resulting from the exotherm of the reaction; oxidation of the beryllium because, unlike most metals, beryllium floats on the reaction slag and is not protected from oxygen; and the viscous nature of the magnesium fluoride slag at the melting point of beryllium making complete metal collection difficult.

In commercial practice (13), about 70% of the stoichiometric magnesium is used. This gives an excess of beryllium fluoride principally to provide a fluid slag under reduction conditions enabling metal collection. Magnesium metal and beryllium fluoride in the solid form are charged into a graphite crucible at a temperature of about 900°C. When the exothermic reaction is completed, the reaction products are heated to about 1300°C to allow molten beryllium to separate and float on top of the slag. The molten metal and slag are then poured into a graphite-receiving pot where both solidify. The mixed reaction product is then crushed and water-leached in a ball mill. The excess beryllium fluoride quickly dissolves causing disintegration of the reaction mass and liberation of the beryllium as generally spherical pebbles. The leach liquor in this step is continuously passed through the ball mill removing the fine, insoluble magnesium fluoride particles and leaving the beryllium pebble in the mill body. The magnesium fluoride is filtered from the leach water and discarded. The leach water containing the excess beryllium fluoride is recycled to the aqueous portion of the fluoride preparation process. The beryllium pebble contains about 97% beryllium along with entrapped reduction slag and unreacted magnesium metal.

Electrolytic Processes. The electrolytic procedures for both electrowinning and electrorefining beryllium have primarily involved electrolysis of the beryllium chloride *[7787-47-5]*, $BeCl_2$, in a variety of fused-salt baths. The chloride readily hydrolyzes making the use of dry methods mandatory for its preparation (see BERYLLIUM COMPOUNDS). For both ecological and economic reasons there is no electrolytically derived beryllium available in the market-place.

Commercial electrorefining of beryllium has been carried out to obtain a purer metal than the magnesium-reduced beryllium. The most notable purification obtained with respect to iron was specified as 300 ppm maximum, and typically between 100 and 200 ppm Fe as contrasted with the 500–1000 ppm, found in the Mg-reduced beryllium metal. There is, however, no metallurgical advantage to having a metal of improved purity.

Vacuum Melting and Casting. A vacuum melting operation is required for beryllium regardless of its origin. The magnesium-reduced pebble contains trapped slag and unreacted magnesium. The electrolytically derived materials contain entrapped electrolyte not removed by aqueous leaching. Vacuum melting is carried out in induction-heated vacuum furnaces using MgO crucibles and graphite ingot molds. The free magnesium and excess beryllium fluoride or electrolyte vaporize during the melting cycle. Nonvolatiles, such as beryllium oxide, magnesium fluoride, and beryllium carbide *[506-66-1]*, separate from the molten metal as a dross that sinks to and adheres to the bottom of the crucible. The purified metal is poured into ingots weighing about 180 kg. This operation also serves as the recycle point for valuable beryllium scrap such as machining chip and trimmings.

Because beryllium is primarily used as a powder metallurgy product or as an alloying agent, casting technology in the conventional metallurgical sense is not commonly utilized with the pure metal.

Fabrication

Beryllium has a close-packed hexagonal crystal structure. At room temperature there are no slip systems operating in a direction outside the basal plane, which sharply restricts ductility. Extensive attempts to increase ductility by purification have not been successful, apparently because of a degree of covalent bonding along the *c*-axis, although bonding along the *a*-axis is metallic. At temperatures above 200°C beryllium exhibits substantial ductility. Alloying has not as yet been found advantageous and the metal is used alone.

Most beryllium hardware is produced by powder metallurgy techniques achieving fine-grained microstructure having a nearly random crystallographic orientation thus providing a strong material with substantial ductility at room temperature. For some specialized applications, sheet and foil have been rolled from cast beryllium ingot. Such material exhibits an average grain size of 50–100 μm as compared to the typical 12 μm or less of the powder metallurgy products.

Beryllium powder is manufactured from vacuum-cast ingot using impact grinding or jet milling. The casting is first reduced to chip by a machining operation such as lathe turning. The chip is then pneumatically directed against a beryllium target using high pressure, dry air producing a powder of less than 44 μm (325 mesh) after appropriate screening. Finer powders, eg, less than 20 μm, are prepared by ball milling with tungsten carbide or steel balls followed by air classification.

Beryllium powder is consolidated by a variety of powder metallurgy processes to near-full density bodies (99 +% of theoretical density) (see METALLURGY, POWDER). Vacuum hot-pressing of right circular cylinders at 1000–1200°C at 7 MPa (1000 psi) using graphite tooling has been the most commonly used procedure, particularly where large shapes are desired. The pressing sizes that can be produced range from 18 to 183 cm in diameter and 15 to 168 cm in length. The largest pressing made to date weighed approximately 3000 kg.

Hot-isostatic-pressing (HIP) is replacing the vacuum hot-pressing procedure for all but the largest shapes. This process, in the case of beryllium involves loading the beryllium powder into a mild steel can of the desired configuration, outgassing the powder under vacuum, subsequently sealing the can, and applying argon gas pressure to the can in an isostatic manner in a cold-wall pressure vessel having an internal furnace heated to the appropriate temperature. The usual processing conditions for beryllium are 103 MPa (15,000 psi) at 1000°C. The advantages of the HIP process include the economics of consolidating the powder to near the final desired shape as contrasted to the right circular cylinder limitation of the vacuum hot-pressing procedure, a shorter floor-to-floor time for a given shape, essentially full density (at 100% of theoretical), and higher strengths than the hot-pressed material because there is little or no grain growth during the HIP procedure.

Cold-isostatic-pressing followed by vacuum sintering or HIP is also used to manufacture smaller intricate shapes. In this instance beryllium powder is loaded into shaped rubber bags and pressed isostatically in a pressure chamber up to 410 MPa (60,000 psi). After the pressing operation the rubber bag is stripped from the part which is then vacuum sintered to about 99% of theoretical density at about 1200°C. If full theoretical density is required, the sintered part may be simply given a HIP cycle because there is no open porosity after vacuum sintering. In a similar manner, conventional axial cold-pressing

followed by vacuum sintering is commercially used for small (under 1 kg) parts where appropriate.

Beryllium sheet is produced by rolling powder metallurgy billets clad in steel cans at 750–790°C. Beryllium foil down to 12.5 μm (0.0005 in.) in gauge is commercially available. Extrusion is also carried out in this temperature region, again using steel cans to contain the powder metallurgy billet. Working of beryllium results in the establishment of a high degree of preferred crystallographic orientation, generally enhancing the properties in the direction of working, but impairing properties normal to the working direction. This is particularly true for tensile elongation. Cross-rolling schedules are followed in rolling that ensure good tensile elongation in the plane of the sheet (10% minimum by specification and 20% is not unusual), but the strain capacity in the thickness direction is limited. The preferred orientation problem has limited the use of wrought beryllium; many shapes other than common structurals are usually machined from billets where standard metallurgical practice with other metals would involve rolled, extruded, or forged components.

The chemical composition and guaranteed tensile properties of the available commercial grades of beryllium in the vacuum hot-pressed form are summarized in Tables 2 and 3. Other consolidation procedures have similar specification property levels. The S-65 grade is of particular interest in that a room temperature minimum tensile elongation of 3% is guaranteed when tested in any direction. This strain capacity is achieved through control of the beryllium oxide content to less than 1%, control and balancing of impurities such as iron and aluminum, and consolidation by techniques which maximize randomization of the crystallographic texture.

Table 2. Commercial Grades of Vacuum Hot-Pressed Beryllium, Composition by wt

	S-65B	S-200F	I-70A	I-220B	I-400
Be, min %	99.0	98.5	99.0	98.0	94.0
BeO, max %	1.0	1.5	0.7	2.2	4.2[a]
Al, max ppm	600	1000	700	1000	1600
C, max ppm	1000	1500	700	1500	2500
Fe, max ppm	800	1300	1000	1500	2500
Mg, max ppm	600	800	700	800	800
Si, max ppm	600	600	700	800	800
other, each max ppm	400	400	400	400	1000

[a] Percentage of BeO specified is minimum in this instance.

Table 3. Tensile Properties of Beryllium Commercial Grades at Ambient Temperatures[a]

	S-65B	S-200F	I-70A	I-220B	I-400
tensile strength, min MPA[b]					
ultimate	290	324	241	379	345
yield strength[c]	207	241	172	276	
elongation, min %	3	2	2	2	
microyield, min MPa[b]		27	12	34	62

[a] Young's Modulus is 303 GPa (4.4 × 10^7 psi) and the Poisson's ratio 0.07.

[b] To convert MPa to psi, multiply by 145.

[c] 0.2% offset.

Economic Aspects

The largest consumption of beryllium is in the form of alloys, principally the copper–beryllium series. The consumption of the pure metal has been quite cyclic in nature depending on specific governmental programs in armaments, nuclear energy, and space. The amount of beryllium extracted from bertrandite has ranged between 200 and 270 metric tons per year since 1986 (14). Small quantities of beryl were also processed during this period.

The price of beryllium oxide powder was $154 kg in 1991. The beryllium content of copper–beryllium master alloy was $352 kg. Pure beryllium powder was priced at $615 kg whereas simple shapes in vacuum hot-pressed material were priced at about $685 kg in 1991.

Analysis

Instrumental methods such as atomic absorption and emission spectrometry, and gamma activation are employed in most beryllium determinations; however, gravimetric and tritrimetric methods remain useful when high accuracy is required.

Beryllium in reference standards is determined by precipitation of beryllium hydroxide using ammonia. The precipitate is ignited to beryllium oxide and weighed. Interfering elements that precipitate must be removed or masked. Excess ammonia minimizes coprecipitation of manganese, cobalt, copper, nickel, and zinc. Ethylenedinitrilo tetraacetate (EDTA) minimizes precipitation of aluminum, chromium, and iron and further reduces coprecipitation of manganese, cobalt, copper, nickel, and zinc. Alternatively, aluminum, iron, titanium, zirconium, cobalt, nickel, copper, cadmium, and zinc can be removed by precipitation with 8-hydroxyquinoline prior to addition of ammonia. Fluoride, citrate, and tartrate prevent complete precipitation of beryllium and must be absent. Fluoride can be removed by strong fuming in sulfuric acid; phosphate can be removed by precipitation with ammonium molybdate; and silica contamination of the ignited beryllium oxide can be eliminated by adding sulfuric and hydrofluoric acids to the crucible, fuming to dryness, and re-igniting to constant weight (15,16).

Assay of beryllium metal and beryllium compounds is usually accomplished by titration. The sample is dissolved in sulfuric acid. Solution pH is adjusted to 8.5 using sodium hydroxide. The beryllium hydroxide precipitate is redissolved by addition of excess sodium fluoride. Liberated hydroxide is titrated with sulfuric acid. The beryllium content of the sample is calculated from the titration volume. Standards containing known beryllium concentrations must be analyzed along with the samples, as complexation of beryllium by fluoride is not quantitative. Titration rate and hold times are critical; therefore use of an automatic titrator is recommended. Other fluoride-complexing elements such as aluminum, silicon, zirconium, hafnium, uranium, thorium, and rare earth elements must be absent, or must be corrected for if present in small amounts. Copper–beryllium and nickel–beryllium alloys can be analyzed by titration if the beryllium is first separated from copper, nickel, and cobalt by ammonium hydroxide precipitation (15,16).

Beryllium alloys are usually analyzed by optical emission or atomic absorption spectrophotometry. Low voltage spark emission spectrometry is used for the analysis of most copper–beryllium alloys. Spectral interferences, other inter-element effects, metallurgical effects, and sample inhomogeneity can degrade accuracy and precision and must be considered when constructing a method (17).

Inductively coupled argon plasma (icp) and direct current argon plasma (dcp) atomic emission spectrometry are solution techniques that have been applied to copper–beryllium, nickel–beryllium, and aluminum–beryllium alloys, beryllium compounds, and process solutions. The internal reference method, essential in spark source emission spectrometry, is also useful in minimizing drift in plasma emission spectrometry (17). Electrothermal (graphite

furnace) atomic absorption spectrophotometry is employed if the beryllium concentration is very low (17–19).

The commercial ores, beryl and bertrandite, are usually decomposed by fusion using sodium carbonate. The melt is dissolved in a mixture of sulfuric and hydrofluoric acids and the solution is evaporated to strong fumes to drive off silicon tetrafluoride, diluted, then analyzed by atomic absorption or plasma emission spectrometry. If sodium or silicon are also to be determined, the ore may be fused with a mixture of lithium metaborate and lithium tetraborate, and the melt dissolved in nitric and hydrofluoric acids (17).

Metallic impurities in beryllium metal were formerly determined by d-c arc emission spectrography, following dissolution of the sample in sulfuric acid and calcination to the oxide (16) and this technique is still used to determine less common trace elements in nuclear-grade beryllium. However, the common metallic impurities are more conveniently and accurately determined by d-c plasma emission spectrometry, following dissolution of the sample in a hydrochloric–nitric–hydrofluoric acid mixture. Thermal neutron activation analysis has been used to complement d-c plasma and d-c arc emission spectrometry in the analysis of nuclear-grade beryllium.

The methods of choice for beryllium oxide in beryllium metal are inert gas fusion and fast neutron activation. In the inert gas fusion technique, the sample is fused with nickel metal in a graphite crucible under a stream of helium or argon. Beryllium oxide is reduced, and the evolved carbon monoxide is measured by infrared absorption spectrometry. Beryllium nitride decomposes under the same fusion conditions and may be determined by measurement of the evolved nitrogen. Oxygen may also be determined by activation with 14 MeV neutrons (20). The only significant interferents in the neutron activation technique are fluorine and boron, which are seldom encountered in beryllium metal samples.

Total carbon in beryllium is determined by combustion of the sample, along with an accelerator mixture of tin, iron, and copper, in a stream of oxygen (15,16). The evolved carbon dioxide is usually measured by infrared absorption spectrometry. Beryllium carbide can be determined without interference from graphitic carbon by dissolution of the sample in a strong base. Beryllium carbide is converted to methane, which can be determined directly by gas chromatography. Alternatively, the evolved methane can be oxidized to carbon dioxide, which is determined gravimetrically (16).

Chlorine and fluorine in beryllium metal are isolated by pyrohydrolysis or by distillation (21). Fluoride and chloride in the condensate are determined by ion-selective electrode or colorimetrically.

The gamma activation (photoneutron) method is virtually interference-free and applicable to all types of samples. The sample is irradiated with gamma rays from an ^{124}Sb source and emitted neutrons are counted by detectors arrayed around the sample. The neutron flux is proportional to the beryllium content of the sample. A nearly linear response from 0.01 to 100% beryllium is obtained using 25 grams of sample and counting times of 200 seconds. The method is nondestructive, rapid, and requires minimal sample preparation. Minor interferences result from very high concentrations of neutron- or gamma-absorbing elements. Solid and liquid samples can both be analyzed directly; however, sample geometry is critical. Heavy lead shielding is needed to protect the operator. The source, which requires a license in the United States, must be replaced several times per year to maintain a satisfactory counting rate (22,23).

Environmental and biological samples are usually analyzed for beryllium by atomic absorption, using a nitrous oxide–acetylene flame for high concentrations and the graphite furnace for low concentrations. Organic matter in biological samples and air samples collected on filter paper is removed by wet ashing with an oxidizing acid mixture. If refractory beryllium oxide is present, hydrofluoric acid is added to complete its dissolution. Plasma emission spectrometry offers beryllium detection limits that are nearly as good as graphite furnace atomic absorption, as well as reduced interferences and multielement capability. Beryllium in environmental samples has also been converted to volatile complexes for determination by gas chromatography, but this technique has not achieved widespread use (17,24,25).

Spectrophotometric and fluorometric reagents, once used extensively for determination of beryllium (26,27), are seldom employed. Reviews of beryllium analysis are available (15–17,24–30).

Safe Handling

Beryllium, beryllium-containing alloys, and beryllium oxide ceramic in solid or massive form present no hazard whatsoever (31). Solid shapes may be safely handled with bare hands (32); however, care must be taken in the fabrication and processing of beryllium products to avoid inhalation of airborne beryllium particulate matter such as dusts, mists, or fumes in excess of the prescribed workplace exposure limits. Inhalation of fine airborne beryllium may cause chronic beryllium disease, a serious lung disease in certain sensitive individuals. However, the vast majority of people, perhaps as many as 99%, do not react to beryllium exposure at any level (33). The biomedical and environmental aspects of beryllium have been summarized (34).

Safe Exposure Levels. The U.S. Occupational Safety and Health Administration (OSHA) has adopted workplace exposure limits designed to keep airborne concentrations well below the levels known to cause health problems (35) including: (1) daily time-weighted average (TWA) exposure over an eight-hour day is not to exceed beryllium concentrations of 2 μg m^3 of air; and (2) short-term exposure should not exceed beryllium concentrations of 25 μg m^3 of air for a thirty-minute period (36). To protect the general public from environmental exposure to airborne beryllium, the U.S. Environmental Protection Agency has established a beryllium standard of 10 g d as a permissible emission into the air surrounding a plant (37).

Proven Control Measures. Experience has shown that risks in the occupational environment can be economically controlled (38). Operations capable of generating airborne beryllium particulate, such as melting, machining, welding, grinding, etc, are effectively controlled by local exhaust ventilation or other control measures. To assure a safe environment and measure compliance with the OSHA standards, employee exposures should be periodically measured by prescribed air sampling and analytical methods.

Recycling. Beryllium is typically recycled, thus it is not a waste disposal problem; in fact, it is rarely a waste product at all. Because of the high cost of producing beryllium, beryllium producers repurchase clean scrap from customers for recycling and reuse.

Uses

The applications for beryllium center around its nuclear and thermal properties, uniquely high specific modulus or stiffness considered on a weight basis, and excellent dimensional stability along with good machinability. These properties are all combined with a relatively high melting point for a light metal. Beryllium is used extensively as a radiation window, both in source and detector applications, because of its ability to transmit radiation, particularly low energy x-rays. Although it is considered a moderator material for neutrons in nuclear reactors, its actual usage has been in nuclear weapons and as a neutron reflector in high flux test reactors.

Beryllium is used in the space shuttle orbiter as window frames, umbilical doors, and the navigation base assembly. An important application for beryllium is inertial guidance components for missiles and aircraft. Here the lightweight, high elastic modulus, dimensional stability, and the capability of being machined to extremely close tolerances are all important.

Beryllium is important as a sensor support material in advanced fire-control and navigation systems for military helicopters and fighter aircraft utilizing the low weight and high stiffness of the material to isolate instrumentation from vibration. It is also used for scanning mirrors in tank fire-control systems.

Beryllium is used in satellite structures in the form of both sheet and extruded tubing and is a very important material for all types of space optics. Beryllium oxide ceramic applications take advantage of high room temperature thermal conductivity, very low electrical conductivity, and high transparency to microwaves in microelectronic substrate applications.

Alloys Containing Beryllium

A small beryllium addition produces strong effects in several base metals. In copper and nickel this alloying element promotes strengthening through precipitation hardening. In aluminum alloys a small addition improves oxidation resistance, castability, and workability. Other advantages are produced in magnesium, gold, and zinc. Many other alloying compositions have been researched (39), but no alloy with commercial importance approaching these dilute alloys has emerged.

COPPER-BERYLLIUM ALLOYS

Wrought copper–beryllium alloys rank high among copper alloys in attainable strength and, at this high strength, useful levels of electrical and thermal conductivity are retained (see COPPER ALLOYS). Applications include uses in electronic components where their strength-formability-elastic modulus combination leads to use as electronic connector contacts (40); electrical equipment where fatigue strength, conductivity, and thermal relaxation resistance leads to use as switch and relay blades; control bearings where antigalling features are important; housings for magnetic sensing devices where low magnetic susceptibility is critical; and resistance welding systems where hot-hardness and conductivity are important in structural components.

Hardness, thermal conductivity, and castability are important in most casting alloy applications. For example, casting alloys are used in molds for plastic component production where fine cast-in detail such as wood or leather texture is desired. These alloys are also used for thermal management in welding equipment, waveguides, and mold components such as core pins. High strength alloys are used in sporting equipment such as investment cast golf club heads. Castmaster alloys of beryllium in copper, nickel, and aluminum are used in preparing casting alloys or otherwise treating alloy melts.

Because these alloys are precipitation hardenable, they can be customized for specific requirements across a wide range of property combinations. Advances in composition control, processing, and recycling technology have broadened the capabilities and expanded the range of application. Data sheets published by the manufacturers and others (41) give compositions, properties, and typical applications.

Composition and Properties. Commercial wrought copper–beryllium alloys contains 0.2–2.0 wt % beryllium, and 0.2–2.7 wt % cobalt *[7440-48-4]* or up to 2.2 wt % nickel *[7440-02-0]*, in copper *[7440-50-8]*. Casting alloys are somewhat richer, having up to 2.85 wt % beryllium. Within this composition window, two distinct classes, which are referred to as the "high strength" alloys, and the "high conductivity" alloys, are available. Beryllium in the high strength alloys imparts a gold luster whereas the high conductivity alloys appear reddish, like copper, in color. Compositions and physical properties of these alloys are given in Table 4.

Table 4. Physical Properties of Cast and Wrought Beryllium Copper Alloys

Alloy	Constituents, wt %[a]		Density, g/mL	Elastic modulus GPa[b]	Thermal expansion coefficient, ppm/°C[c]	Thermal conductivity, W/(m·K)	Melting range, °C
	Be	Co					
				Wrought alloys			
C17200	1.80–2.00	0.25	8.36	131	17	105	870–980
C17300[d]	1.80–2.00	0.25	8.41	131	17	105	890–1000
C17510[e]	0.26–0.6		8.83	138	18	240	1000–1070
C17410	0.15–0.50	0.5	8.80	138	18	230	1020–1070
				Cast alloys			
C82500[f]	1.90–2.25	0.4	8.30	130	18	97	870–970
C82800[f]	2.50–2.85	0.4	8.14	130	18	90	850–930
C82800[e]	0.35–0.80		8.83	140	18	195–250	1040–1080

[a] The remainder is copper and residual elements. Values are nominal unless range is shown.

[b] To convert from GPa to psi, multiply by 1.45×10^6.

[c] From 20 to 200°C

[d] Also contains 0.25 wt % Pb.

[e] Contains 1.7 wt % Ni and no cobalt.

[f] Also contains 0.25 wt % Si.

Alloy C17200 is foremost among the wrought high strength alloys in industrial importance. A free-machining version, containing a small lead addition to C17200 and available only as rod and wire, is designated C17300. The traditional wrought high conductivity alloys contain 0.2–0.7 wt % Be and up to 2.5 wt % Co or Ni. The newest high conductivity alloy is C17410, having up to 0.4 wt % Be and 0.6 wt % Co. The high strength casting alloys contain 1.6–2.85 wt % Be, nominally 0.5 wt % Co, and a small silicon addition. A minor titanium addition or increased cobalt content are used for grain refinement. The high conductivity casting alloys contain up to 0.8 wt % Be. In all cases the third element addition, either cobalt or nickel, is needed to restrict grain growth during annealing by establishing a dispersion of beryllide particles in the matrix.

Thermal Treatments. The copper–beryllium alloys are classic precipitation strengthening systems. Hardening occurs because the solubility of beryllium is much less at low temperatures than at higher temperatures. In practice, the hardening process is conducted in two steps: solution treatment, commonly called solution annealing or simply annealing, followed by precipitation hardening, also known as age hardening. Some users of the alloys prefer to do the age hardening themselves after part forming.

Solution annealing consists of heating below the solidus temperature to dissolve beryllium in the copper matrix, then rapidly quenching to room temperature to retain beryllium in supersaturated solid solution. The high strength alloys are typically annealed in the range 760–800°C and the high conductivity alloys in the range of 900–955°C. It is not necessary to hold the metal at the annealing temperature for more than a few minutes to affect solution treatment. As a guide, thin strip or wire are annealed in under two minutes, heavy section products, once they reach the annealing temperature, are usually held at temperature for 30 min or less. In this state the alloy is soft and highly workable and therefore may be readily rolled or drawn into strip or wire.

Precipitation hardening involves reheating solution annealed, or solution annealed and cold-worked, material for a time sufficient to nucleate and grow the submicroscopic beryllium-rich precipitates responsible for hardening. For the high strength alloys, age hardening is typically performed in the range of 260–400°C for 0.1–4 h. The high conductivity alloys are age hardened in the range of 425–565°C for 0.5–8 h. Cold-work between solution annealing and hardening increases both the magnitude and rate of strengthening response for wrought products. Up to 37% cold-work, imparted by cold-rolling or drawing, can be provided in commercial products.

During the precipitation process, strength increases, passes through a peak, then decreases more gradually, ultimately reaching a steady-state level. Electrical conductivity is lowest in the solution annealed condition because of the beryllium dissolved in the copper matrix. During age hardening, electrical conductivity increases steadily as dissolved beryllium precipitates. Characteristic curves describing this behavior at various hardening temperatures are useful in process control.

The mechanical and electrical properties of selected high strength alloys in cast and wrought forms are provided in Table 5. A similar compilation for the high conductivity alloys is given in Table 6. The mechanical properties shown in the tables correspond to standard hardening times and temperatures and therefore are close to peak conditions. Considerable latitude exists for achieving a wide variety of special mechanical and electrical property combinations.

Table 5. Properties of Cast and Wrought High Strength Beryllium Copper Alloys

Temper	Yield strength 0.2% offset, MPa[a]	Ultimate tensile strength, MPa[a]	Elongation % in 50.8 mm	Rockwell hardness	Electrical conductivity,[b] IACS %
Wrought alloy C17200					
annealed	190–250	410–530	35–65	B45–78	15–19
cold-rolled	620–800	680–830	2–18	B95–102	15–19
annealed age hardened[c]	960–1210	1130–1350	3–15	C36–42	22–28
cold-rolled age hardened[d]	1130–1420	1310–1520	1–6	C38–45	22–28
annealed mill hardened	480–660	680–760	16–30	B95–C23	17–28
cold-rolled mill hardened	1030–1250	1200–1320	3–12	C33–42	17–28
Cast alloy C82500					
as-cast	280–345	520–590	15–30	B80–85	
cast aged[e]	480–520	690–720	10–20	C20–23	18–25
annealed aged[e,f]	830–1030	1030–1210	1–3	C38–43	18–25
Cast alloy C82800					
as-cast	345–410	590–620	5–25	B80–90	
cast aged[e]	410–480	655–720	10–15	C20–25	17–23
annealed aged[e,f]	1140–1240	1240–1340	0.5–3	C43–47	17–23

[a] To convert MPa to psi, multiply by 145.

[b] IACS International Annealed Copper Standard.

[c] Precipitation heat treatment of 3 h at 315°C.

[d] Precipitation heat treatment of 2 h at 315°C.

[e] Precipitation heat treatment of 3 h at 340°C.

[f] Annealed, then heat treated.

Table 6. Properties of Cast and Wrought High Conductivity Beryllium Copper Alloys

Temper	Yield strength 0.2% offset, MPa[a]	Ultimate tensile strength, MPa[a]	Elongation, % in 50.8 mm	Rockwell hardness	Electrical conductivity,[b] IACS %
Wrought alloy C17510					
annealed	130–210	240–380	20–40	B20–45	20–30
cold-rolled	370–560	480–590	2–10	B78–88	20–30
annealed age hardened[c]	550–690	680–900	10–25	B92–100	45–60
cold-rolled age hardened[c]	650–870	750–940	8–20	B95–102	48–60
Wrought alloy C17410					
cold-rolled mill hardened	650–870	750–900	7–17	B95–C27	45–55
Cast alloy C82200					
as-cast	150–240	310–410	15–25	B50–65	
cast aged[d]	170–380	380–520	10–20	B65–90	45–50
annealed aged[d,e]	480–550	620–760	3–15	B92–100	45–50

[a] To convert MPa to psi, multiply by 145.

[b] See Table 5.

[c] Precipitation heat treatment of 2–3 h at 480°C or hardened at mill.

[d] Precipitation heat treatment of 3 h at 340°C.

[e] Annealed, then heat treated.

Melting, Casting, and Hot Working. The first step in the manufacture of copper–beryllium is production of a nominally 4 wt % Be master alloy by carbothermic reduction of beryllium oxide under molten copper in an electric arc furnace. This master alloy is remelted in coreless induction furnaces and diluted with additional copper, cobalt or nickel, and recycled scrap to adjust the final composition. Melts are directly chill-cast into rectangular or round billets for hot-working to wrought product forms or are poured as ingots for remelting into cast products. The semicontinuously cast rectangular billets are hot-rolled to plate or to coils of hot band for conversion to strip. Round billets are hot-extruded to bar, seamless tube, or rod coil. Hot-working temperatures typically coincide with solution annealing temperatures; about 705–815°C for the high strength alloys and about 815–925°C for the high conductivity alloys. Hot-worked products are softened as needed by solution annealing before further processing.

Finishing. Subsequent processing of wrought copper–beryllium alloys typically includes one or more cycles of cold-working and intermediate solution annealing. Chemical cleaning is performed after each anneal. Processing after the final anneal may include cold-rolling, heat treatment to specified strength levels (mill hardening), and, for strip, slitting to specified width. Wrought products are also treated with corrosion inhibiting films to extend shelf life. During manufacture, mill products are monitored for stringent control of as-cast composition, nonmetallic inclusion content, intermediate and finish annealed grain size, dimensional consistency, as-shipped mechanical properties, age hardening response, and surface condition.

Cast Products. The copper–beryllium alloys can be melted in resistance, gas, induction, and electric arc furnaces. Induction furnaces, in particular, allow close control of melt temperature and agitation to minimize gas absorption, beryllium loss, and dross formation. Drossing is minimized by melting under inert gas or in air melting by use of a graphite cover. Furnace refractories suitable for melting copper–beryllium casting alloys include clay graphite, silicon carbide, alumina, magnesia, and zirconia. High silica refractories may react with copper–beryllium melts. Most common casting methods for copper-base alloys are applicable to copper–beryllium. These include pressure casting, investment casting, centrifugal casting, the Shaw process, die casting, and casting in permanent, ceramic, and various types of sand molds. Shrinkage is similar to tin bronze and less than that of aluminum, silicon, or manganese bronze. Metal or graphite chills may be placed in sand molds to promote directional solidification and reduce shrinkage porosity.

Impurities above maximum levels indicated in published specifications (42) can affect the properties of the finished casting. Silicon, for example, is normally added to many of the copper–beryllium casting alloys to promote fluidity, but excess silicon reduces ductility. Excessive zinc, tin, phosphorus,

lead, and chromium behave similarly. Aluminum and iron reduce age hardening response, and degrade electrical and thermal properties.

NICKEL–BERYLLIUM ALLOYS

Dilute alloys of beryllium in nickel, like their copper–beryllium counterparts, are age hardenable (43). Nickel–beryllium alloys are distinguished by very high strength; good bend formability in strip; and high resistance to fatigue, elevated temperature softening, stress relaxation, and corrosion. Wrought nickel–beryllium is available as strip, rod, and wire and is used in mechanical, electrical, and electronic components that must exhibit good spring properties at elevated temperatures. Examples include thermostats, bellows, as well as pressure sensing diaphragms and burn-in connectors and sockets.

A variety of nickel–beryllium casting alloys exhibit strengths nearly as high as the wrought products with castability advantages. Casting alloys are used in molds and cores for glass and plastic molding, and in jewelry and dental applications by virtue of their high replication of detail in the investment casting process.

Composition and Properties. A single composition, UNS NO3360, is supplied in wrought form. Nickel–beryllium casting alloys include 6 wt % Be master alloy, a series with 2.2–2.6 wt % Be including one with a minor carbon addition for enhanced machinability, and a series of ternary nickel-base alloys with up to 2.75 wt % Be and 12 wt % Cr. Composition and physical properties of several of these alloys are presented in Table 7; mechanical properties are given in Table 8. Although displaying only a fraction of the conductivity of copper–beryllium, nickel–beryllium exceeds the conductivity of stainless steel and most other nickel-base alloys by a factor of two to three because of its relatively low total alloy content.

Table 7. Properties of Cast and Wrought Beryllium Nickel Alloys[a]

Alloy[c]	Constituents, wt %[b]		Density, g mL	Elastic modulus, GPa[d]	Thermal expansion coefficient, ppm °C[e]	Thermal conductivity, W (m·K)	Melting range, °C
	Be	Other					
NO3360[f]	1.80–2.05	0.5 Ti	8.27	195–210	4.5	28	1195–1325
M220C	2.0	0.5 C	8.08–8.19	179–193	4.8	36.9[g] 51.1[h]	1150 (solidus)
42C	2.75	12.0 Cr	7.8	193		34.6[i]	1165 (solidus)

[a] Tabulated properties apply to age hardened products.

[b] The remainder is nickel and residual elements. Nominal unless range is shown.

[c] Alloy is cast unless otherwise indicated.

[d] To convert GPa to psi, multiply by 1.45×10^6.

[e] From 20 to 550°C.

[f] Wrought alloy.

[g] At 38°C.

[h] At 538°C.

[i] At 93°C.

Table 8. Properties of Cast and Wrought Beryllium Nickel Alloys

Temper	Heat treatment,[a] h	Yield strength 0.2% offset, MPa[b]	Ultimate tensile strength, MPa[b]	Elongation, % in 50.8 mm[c]	Rockwell hardness	Electrical conductivity, IACS %[c,d]
Wrought alloy NO3360						
annealed		275–485	655–895	30	A39–57	4
cold-rolled		1035–1310	1065–1310	1	A55–75	4
annealed age hardened	2.5	1035[c]	1480[c]	12	15N78–86	6
cold-rolled age hardened	1.5	1585[c]	1860[c]	8	15N83–90	6
mill hardened		690–860	1065–1240	14		5
mill hardened		1515–1690	1790–2000	8		5
Cast alloy M220C						
annealed		345[c]	760[c]	35	B95[c]	
annealed age hardened	3	1380[c]	1620[c]	4	C54[c]	
Cast alloy 42C						
annealed age hardened	3		1034[c]	6	C38[c]	5

[a] Time given is at 510°C.

[b] To convert from MPa to psi, multiply by 145.

[c] Value given is minimum value.

[d] See Table 5.

Thermal Treatments. Processing of nickel–beryllium alloys is analogous to processing high strength copper–beryllium. The alloys are solution annealed at a temperature high in the alpha nickel region to dissolve a maximum amount of beryllium, then rapidly quenched to room temperature to create a supersaturated solid solution. Precipitation hardening involves heating to a temperature below the equilibrium solvus to nucleate and grow metastable Be-rich precipitates that harden the matrix. Wrought NO3360 is typically solution annealed at about 1000°C. Cold-work up to about 40% may be imparted between solution annealing and aging to increase the rate and magnitude of the age hardening response. Aging to peak strength is performed

at 510°C, up to 2.5 h for annealed and 1.5 h for cold-worked material. Under-, peak-, and overaging behavior are displayed. The cast binary alloys are solution annealed at about 1065°C and aged at 510°C for three hours. Cast ternary alloys are annealed near 1090°C and given the same aging treatment. Castings are typically used in the solution annealed and aged condition for maximum strength.

Production. Manufacturing of nickel–beryllium products commences with induction melting of a charge consisting of 6% Be–Ni master alloy, additive elements, and recycled scrap. The 6% Be–Ni master is produced by is produced by induction melting commercial purity beryllium and nickel rather than by carbothermic reduction of beryllium oxide as for copper–beryllium master. Rectangular or round billets are semicontinuously cast for hot-working to strip or round products. Hot-rolling and extrusion are performed in the vicinity of the solution annealing temperature, about 980°C. The hot-worked products are brought to a ready-to-finish size by one or more iterations of solution annealing and cold-working. Chemical cleaning is required after each anneal to remove oxide films. A final solution anneal establishes the finished grain size and age hardening response. Cold-working and mill age hardening may follow the final anneal.

Nickel–beryllium casting alloys are readily air melted, in electric or induction furnaces. Melt surface protection is supplied by a blanket of argon gas or an alumina-base slag cover. Furnace linings or crucibles of magnesia are preferred, with zirconium silicate or mullite also adequate. Sand, investment, ceramic, and permanent mold materials are appropriate for these alloys. Beryllium in the composition is an effective deoxidizer and scavenger of sulfur and nitrogen.

BERYLLIUM IN ALUMINUM ALLOYS

Small additions of beryllium to aluminum systems are known to improve consistency (44). When as little as 0.005–0.05 wt % beryllium is added as a master alloy to an aluminum alloy during melting, a protective surface oxide film is formed. This film reduces drossing, increases cleanliness, and improves fluidity. Preferentially oxidizable alloy additions such as magnesium and sodium are protected from oxidation during melting and casting. Hydrogen absorption is also reduced as are mold reactions. Castings thus have improved surface finish, consistent strength, and higher ductility. Additional benefits cited include reduced tarnishing, improved buffing and polishing response, and consistency of aging response, particularly in alloys containing magnesium or silicon. Applications include aircraft skin panels and aircraft structural castings in alloy A357.

Beryllium and aluminum are virtually insoluble in one another in the solid state. The potential therefore exists for an aluminum–beryllium metal matrix composite with lower density and higher elastic modulus, ie, improved specific modulus, than conventional aluminum alloys produced by ingot or powder metal processing. At least one wrought composite system with nominally 62 wt % Be and 38 wt % Al has seen limited use in aerospace applications (see COMPOSITES).

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BERYLLIUM COMPOUNDS

Beryllium Carbide. Beryllium carbide *[506-66-1]*, Be_2C, may be prepared by heating a mixture of beryllium oxide and carbon to 1950–2000°C, or heating a blend of beryllium and carbon powders to 900°C under mechanical pressure of 3.5–6.9 MPa (500–1000 psi). The metal–carbon reaction is easier to carry out and is accompanied by a substantial exotherm. The reaction mass is quite friable and readily converted to a powder for consolidation by hot pressing at temperatures on the order of 1800°C.

Beryllium carbide slowly hydrolyzes to beryllium oxide and methane in the presence of atmospheric moisture although months may be required to complete the reaction. Any carbon contained in beryllium metal is present as the carbide because the solubility of carbon in beryllium is extremely low.

The crystal structure of beryllium carbide is cubic, density 2.44 g mL. The melting point is 2250–2400°C and the compound dissociates under vacuum at 2100°C (1). This compound is not used industrially, but Be_2C is a potential first-wall material for fusion reactors, one on the very limited list of possible candidates (see FUSION ENERGY).

Beryllium Carbonates. Beryllium carbonate tetrahydrate *[60883-64-9]*, $BeCO_3 \cdot 4H_2O$, has been prepared by passing carbon dioxide through an aqueous suspension of beryllium hydroxide. It is unstable and is obtained only when the solution is under carbon dioxide pressure. Beryllium oxide carbonate *[66104-25-4]* is precipitated when sodium carbonate is added to a beryllium salt solution. Carbon dioxide is evolved. The precipitate appears to be a mixture of beryllium hydroxide and the normal carbonate, $BeCO_3$, and usually contains two to five molecules of $Be(OH)_2$ for each $BeCO_3$.

Soluble beryllium carbonate complexes are produced by dissolving beryllium oxide carbonate or hydroxide in ammonium carbonate. Iron and aluminum hydroxides are insoluble in this solution; hence, the reaction can be used to separate these two elements from beryllium. The resulting solution appears to approach the stoichiometry of a solution of tetraammonium beryllium tricarbonate *[65997-36-6]*, $(NH_4)_4Be(CO_3)_3$. After removal of insoluble impurities, hydrolysis of $(NH_4)_4Be(CO_3)_3$ just below the boiling point gives a granular precipitate of di(beryllium carbonate) beryllium hydroxide *[66104-24-3]*, $2BeCO_3 \cdot Be(OH)_2$, which can be dried to constant weight at 100°C. Decomposition to BeO is nearly complete after five days at 200°C. The continued addition of $2BeCO_3 \cdot Be(OH)_2$ and $(NH_4)_2CO_3$ to a warmed solution of $(NH_4)Be(CO_3)_3$ has produced solutions containing up to 42 g L Be in which the empirical composition is $(NH_4)_2Be(CO_3)_2$. The solid beryllium oxide carbonate intermediates are obtained by a laboratory procedure for preparing pure beryllium salt solutions by reaction with aqueous mineral or organic acids.

Beryllium Carboxylates. The beryllium salts of organic acids can be divided into normal carboxylates, $Be(RCOO)_2$, and beryllium oxide carboxylates, $Be_4O(RCOO)$. The latter are prepared by dissolving beryllium oxide, hydroxide, or the oxide carbonate in an organic acid, followed by evaporation to give either a solid or an oily liquid. The oxide carboxylate is extracted using chloroform or petroleum ether and recrystallized from the solvent. These compounds are nonelectrolytes, soluble in organic solvents, insoluble in cold water, possess sharp melting points, and can usually be sublimed or distilled without decomposition. The oxide formate requires special preparation by heating the normal formate to 250–260°C or by boiling it with a water suspension containing the calculated amount of beryllium oxide carbonate. The normal beryllium carboxylates must be prepared under strictly anhydrous conditions. The normal acetate is made by treating the oxide acetate with glacial acetic acid and acetyl chloride.

Beryllium Halides. The properties of the fluoride differ sharply from those of the chloride, bromide, and iodide. Beryllium fluoride is essentially an ionic compound, whereas the other three halides are largely covalent. The fluoroberyllate anion is very stable.

Beryllium fluoride *[7787-49-7]*, BeF_2, is produced commercially by the thermal decomposition of diammonium tetrafluoroberyllate *[14874-86-3]*, $(NH_4)_2BeF_4$. The fluoride and the fluoroberyllates show a strong similarity to silica and the silicates. Like silica, beryllium fluoride readily forms a glass, which on heating above 230°C crystallizes spontaneously to give the quartz modification. This quartz modification exists in two forms: the low temperature α-form is converted to the high temperature β-form at 227°C. The melting point of the quartz form of beryllium fluoride appears to be 552°C (2).

Beryllium fluoride is hygroscopic and highly soluble in water, although its dissolution rate is slow. Fluoroberyllates can be readily prepared by crystallization or precipitation from aqueous solution. Compounds containing the BeF^2 ion are the most readily obtained, though compounds containing other fluoroberyllate ions can also be obtained, eg, NH_4BeF_3, depending upon conditions.

Beryllium chloride *[7787-47-5]*, $BeCl_2$, is prepared by heating a mixture of beryllium oxide and carbon in chloride at 600–800°C. At pressures of 2.7–6.7 Pa (0.02–0.05 mm Hg) beryllium chloride sublimes at 350–380°C. It is easily hydrolyzed by water vapor or in aqueous solutions. Beryllium chloride hydrate *[14871-75-1]* has been obtained by concentrating a saturated aqueous solution of the chloride in a stream of hydrogen chloride. Chloroberyllate compounds have not been isolated from aqueous solutions, but they have been isolated from anhydrous fused salt mixtures.

Beryllium bromide *[7787-46-4]*, $BeBr_2$, and beryllium iodide *[7787-53-3]*, BeI_2, are prepared by the reaction of bromine or iodine vapors, respectively, with metallic beryllium at 500–700°C. They cannot be prepared by wet methods. Neither compound is of commercial importance and special uses are unknown.

Beryllium Hydride. Beryllium hydride *[7787-52-2]*, BeH_2, is best prepared by the controlled pyrolysis of di-*t*-butyl beryllium *[20841-21-7]*, $C_8H_{18}Be$, at 200°C. Pressure densification of the amorphous pyrolysis product yields 96% pure crystalline BeH_2 having a density near 0.6 g mL. Di-*t*-butyl beryllium is prepared by the reaction, in ether, of $BeCl_2$ and *t*-butyl-Grignard reagent, *t*-(C_4H_9)–MgCl (see GRIGNARD REACTION). Metallic beryllium does not react with hydrogen directly to give the hydride (3). Thermally stable to 240°C, crystalline beryllium hydride is resistant to attack by water and common organic solvents. Interest in beryllium hydride has centered on its potential use as a solid propellant rocket fuel. Theoretically, BeH_2 has the highest specific impulse of any fuel material except solid hydrogen.

Beryllium Hydroxide. Beryllium hydroxide *[13327-32-7]*, $Be(OH)_2$, exists in three forms. On addition of alkali to a beryllium salt solution to obtain a slightly basic pH, a slimy, gelatinous beryllium hydroxide is produced. Aging this amorphous product results in a metastable tetragonal crystalline form, which after months of standing transforms into a stable orthorhombic crystalline form. The orthorhombic modification is also precipitated from a sodium beryllate solution containing more than 5 g L Be by hydrolysis near the boil. This granular beryllium hydroxide is the readily filtered product from the sulfate extraction processing of beryl to obtain metallic beryllium. When heated, beryllium hydroxide loses water. Most of the water comes off in the 600–700°C region, but temperatures on the order of 950°C are required for complete dehydration to the oxide. There is evidence that beryllium hydroxide exists in the vapor phase above 1200°C (4). Water vapor reacts with BeO to form beryllium hydroxide vapor, which has a partial pressure of 73 Pa (0.55 mm Hg) at 1500°C.

Beryllium Intermetallic Compounds. Beryllium forms intermetallic compounds, referred to as beryllides, with most metals. They are usually prepared by a solid-state reaction of the blended powder constituents at about 1260°C. Fabrication of the reacted powders into specific shapes is carried out by standard powder metallurgical techniques such as vacuum hot pressing or hot isostatic pressing (see METALLURGY, POWDER). The properties exhibited by some beryllides include excellent oxidation resistance, high strength at elevated temperature, good thermal conductivity, and low densities as compared with refractory metals and ceramic materials (see CERAMICS; REFRACTORIES). Table 1 lists melting points and densities of some of the more

promising oxidation-resistant beryllides (5).

Table 1. High Temperature Oxidation Resistant Beryllides

Beryllide system	Compound formula	CAS Registry Number	Melting point, °C	X-ray density, g/mL	Be, wt %
hafnium	$HfBe_{13}$		1595	3.93	39.7
	Hf_2Be_{17}		<1750	4.78	30.0
molybdenum	$MoBe_{12}$		ca 1705	3.03	53.2
niobium	$NbBe_{12}$	*[12010-12-7]*	1690	2.92	53.8
	Nb_2Be_{17}	*[12010-34-3]*	1705	3.28	45.2
titanium	$TiBe_{12}$	*[12232-67-6]*	1595	2.26	69.3
	Ti_2Be_{17}		1630	2.46	61.5
tantalum	$TaBe_{12}$	*[12010-13-8]*	1850	4.18	37.4
	Ta_2Be_{17}		1990	5.05	29.8
zirconium	$ZrBe_{13}$	*[12010-33-2]*	1925	2.72	56.2
	Zr_2Be_{17}		1980	3.08	45.7

The beryllides, being intermetallic compounds, are hard, strong materials which exhibit little ductility at room temperature. Strength properties increase gradually as a function of temperature up to about 870°C, above which a sharp increase in strength occurs, peaking in the region of 1260°C; the modulus of rupture values exceed 280 MPa (40,000 psi) at this latter temperature.

Similar to some other intermetallic compounds, most notably molybdeum disilicide *[12136-78-6]*, $MoSi_2$, certain beryllides show anomalous oxidation behavior exhibiting excellent oxidation resistance at high temperature, eg, 1260°C, but little or no oxidation resistance in some lower temperature range. Such behavior was observed in the 700–870°C range for Nb_2Be_{17}, $NbBe_{12}$, Zr_2Be_{17}, and $ZrBe_{13}$, but not for other compounds listed in Table 1 (6). Complete disintegration of the vulnerable beryllides into powder occurred within 24 hours. The addition of small amounts of aluminum *[7429-90-5]* metal, or the nickel–aluminum (1:1) *[12003-78-0]* compound NiAl solved this problem.

The beryllides continue to be of interest for high temperature aerospace applications because of their oxidation resistance, low density, and high strength at elevated temperature (7). The limited strain capacity of the materials, particularly at low temperatures, has thus far prevented actual use.

Beryllium Nitrate. Beryllium nitrate tetrahydrate *[13516-48-0]*, $Be(NO_3)_2 \cdot 4H_2O$, is prepared by crystallization from a solution of beryllium hydroxide or beryllium oxide carbonate in a slight excess of dilute nitric acid. After dissolution is complete, the solution is poured into plastic bags and cooled to room temperature. The crystallization is started by seeding. Crystallization from more concentrated acids yields crystals with less water of hydration. On heating above 100°C, beryllium nitrate decomposes with simultaneous loss of water and oxides of nitrogen. Decomposition is complete above 250°C.

Beryllium Nitride. Beryllium nitride *[1304-54-7]*, Be_3N_2, is prepared by the reaction of metallic beryllium and ammonia gas at 1100°C. It is a white crystalline material melting at 2200°C with decomposition. The sublimation rate becomes appreciable in a vacuum at 2000°C. Be_3N_2 is rapidly oxidized by air at 600°C and like the carbide is hydrolyzed by moisture. The oxide forms on beryllium metal in air at elevated temperatures, but in the absence of oxygen, beryllium reacts with nitrogen to form the nitride. When hot pressing mixtures of beryllium nitride and silicon nitride, Si_3N_4, at 1700°C, beryllium silicon nitride *[12265-44-0]*, $BeSiN_2$, is obtained. $BeSiN_2$ may have application as a ceramic material.

Beryllium Oxalate. Beryllium oxalate trihydrate *[15771-43-4]*, $BeC_2O_4 \cdot 3H_2O$, is obtained by evaporating a solution of beryllium hydroxide or oxide carbonate in a slight excess of oxalic acid. The compound is very soluble in water. Beryllium oxalate is important for the preparation of ultrapure beryllium hydroxide by thermal decomposition above 320°C. The latter is frequently used as a standard for spectrographic analysis of beryllium compounds.

Beryllium Oxide. Beryllium oxide *[1304-56-9]*, BeO, is the most important high purity commercial beryllium chemical. In the primary industrial process, beryllium hydroxide extracted from ore is dissolved in sulfuric acid. The solution is filtered to remove insoluble oxide and sulfate impurities. The resulting clear filtrate is concentrated by evaporation and upon cooling high purity beryllium sulfate, $BeSO_4 \cdot 4H_2O$, crystallizes. This salt is calcined at carefully controlled temperatures between 1150°C and 1450°C, selected to give tailored properties of the beryllium oxide powders as required by the individual beryllia ceramic fabricators. Commercial beryllium oxide powder calcined at 1150°C consists of crystallites predominately 0.1–0.2 μm in size. Powder particles are made up of clusters or aggregates of the smaller crystallites.

Ceramic-grade beryllium oxide has also been manufactured by a process wherein organic chelating agents (qv) were added to the filtered beryllium sulfate solution. Beryllium hydroxide is then precipitated using ammonium hydroxide, filtered, and carefully calcined to obtain a high purity beryllium oxide powder.

High purity beryllium oxide powder is fabricated by classical ceramic-forming processes such as dry pressing, isostatic pressing, extrusion, tape casting, and slip casting. Additives consisting of the oxides of magnesium, aluminum, or silicon, or various combinations are frequently included in the ceramic mixes to improve the reproducibility of sintering and resultant properties. The green compact of formed beryllia is commonly sintered at 1500–1600°C in dry air or dry hydrogen. Moisture in the sintering atmosphere affects the surface characteristics such as roughness, texture, and microstructure (8). The sintering operation produces beryllia ceramics at 95–97% of the theoretical density with an average grain size between 6 and 30 μm. Higher density may be achieved by hot pressing high purity beryllia powder.

Beryllia ceramics offer the advantages of a unique combination of high thermal conductivity and heat capacity with high electrical resistivity (9). Thermal conductivity equals that of most metals; at room temperature, beryllia has a thermal conductivity above that of pure aluminum and 75% that of copper. Properties illustrating the utility of beryllia ceramics are shown in Table 2.

Table 2. Properties of High Purity Beryllium Oxide Ceramics

Property	Value
specific heat, J/(g·K)[a]	1.050
thermal conductivity, W/(m·K)	
at 25°C	290–330
at 100°C	190–220
dielectric constant (loss tangent)	
1 MHz at 25°C	6.55–6.72 (0.00005–0.00016)
1 MHz at 100°C	6.55–6.75 (0.00007–0.00019)

1 GHz at 25°C	6.72–6.75 (0.00006–0.00035)
1 GHz at 100°C	6.72–6.81 (0.00014–0.00051)
9.3 GHz at 25°C	6.77 (0.00007–0.00031)
9.3 GHz at 100°C	6.77 (0.00026–0.00047)
volume resistivity, Ωm	
at 25°C	2.0×10^{14} 1.3×10^{15}
at 100°C	1.4×10^{11} 5.0×10^{11}
coefficient of thermal expansion, K^{-1}	
at 100°C	9.7×10^{-6}
at 500°C	13.3×10^{-6}
tensile strength, MPa[b]	150
compressive strength, MPa[b]	1400
modulus of rupture, MPa[b]	250
modulus of elasticity, GPa[b]	345
Poisson's ratio	0.164–0.380

[a] To convert J to cal, divide by 4.184.

[b] To convert MPa to psi, multiply by 145.

Beryllia ceramic parts are frequently used in electronic and microelectronic applications requiring thermal dissipation (see CERAMICS AS ELECTRICAL MATERIALS). Beryllia substrates are commonly metallized using refractory metallizations such as molybdenum–manganese or using evaporated films of chromium, titanium, and nickel–chromium alloys. Semiconductor devices and integrated circuits (qv) can be bonded by such metallization for removal of heat.

Beryllium Sulfate. Beryllium sulfate tetrahydrate *[7787-56-6]*, $BeSO_4 \cdot 4H_2O$, is produced commercially in a highly purified state by fractional crystallization from a beryllium sulfate solution obtained by the reaction of beryllium hydroxide and sulfuric acid. The salt is used primarily for the production of beryllium oxide powder for ceramics. Beryllium sulfate dihydrate *[14215-00-0]*, is obtained by heating the tetrahydrate at 92°C. Anhydrous beryllium sulfate *[13510-49-1]* results on heating the dihydrate in air to 400°C. Decomposition to BeO starts at about 650°C, the rate is accelerated by heating up to 1450°C. At 750°C the vapor pressure of SO_3 over $BeSO_4$ is 48.7 kPa (365 mm Hg).

Economic Aspects

Beryllium is principally consumed in the metallic form, either as an alloy constituent or as the pure metal. Consequently, there is no industry associated with beryllium compounds except for beryllium oxide, BeO, which is commercially important as a ceramic material. BeO powder is available at $154 kg in 1991.

Safe Handling

Beryllium-containing materials can be potentially harmful if mishandled. Care must be taken in the fabrication and processing of beryllium products to avoid inhalation of airborne beryllium particulate matter such as dusts, mists, or fumes in excess of prescribed work place limits. Inhalation of fine airborne beryllium may cause chronic beryllium disease, a serious lung disorder, in certain sensitive individuals. However, most people, perhaps as many as 99%, do not react to beryllium exposure at any level (see BERYLLIUM AND BERYLLIUM ALLOYS).

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BETA-BLOCKERS.

See CARDIOVASCULAR AGENTS.

BETA-LACTAM ANTIBIOTICS.

See ANTIBIOTICS, β-LACTAMS.

BEVERAGE SPIRITS, DISTILLED

The word alcohol, like alchemy, has its origins in the Middle East. The Arabs are said to have made cosmetic paints by heating and vaporizing a mixture of compounds. The residue was used to paint eyelids and called "kohl." When they later heated wines, they gave the product the same name as the cosmetic "kohl" or "al kohl." The word whiskey is said to be derived from the Celtic "uisge baugh" or "water of life."

Egyptians purportedly practiced distillation around 1000–2000 BC by heating wine and making a product called arden spirits. China and India are also said to have carried out distillation in the pre-Christian era. The Chinese reportedly made a distilled beverage from rice beer around 800 BC. The Arabs learned about distillation from the Egyptians and developed an apparatus in the form of a closed heated container that was called an alembic.

In some of his work, Pliny the Elder (24–79 AD) wrote of the heating of wine with flames. In the tenth century, the Persian philosopher Avicenna (980–1037 AD) described a distillation still. Magister Salernus wrote about "aqua ardens" around 1150 AD. The German alchemist and philosopher, Albertus Magnus (1200–1280 AD), studied wine distillation, made improvements, and wrote a manuscript on the production of aqua ardens.

Study of the alembic continued throughout the sixteenth century. Hieronymus Brunswick wrote *Liber De Arte Distillanti* in 1500 and described various improvements in distillation. Ryff produced a book on advances in the alembic still in Germany in 1556. In the eighteenth century, many further advances were made in the alembic, particularly by the French who worked with fruit brandies as opposed to the thick, grain mashes used by the Germans and English. These improvements are seen in the pot stills of today, used in the production of malt whiskeys in Scotland and brandy in France (Fig. 1).

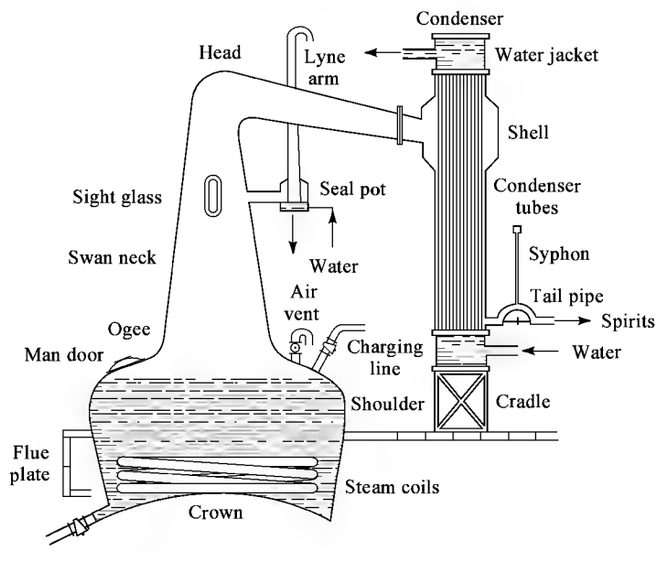

Fig. 1. Pot (batch) still.

In 1801, Edward Adam discovered redistillation or rectification. He designed an apparatus in which vapors pass from the kettle through an egg-shaped vessel into the condenser. Progress in distillation knowledge and equipment continued throughout the nineteenth century. In 1831 Aencas Coffey, in Dublin, Ireland, developed a continuous still that gave faster and lower cost distillations and yielded both higher proofs and a better quality product than the batch process pot still. The Coffey Still (Fig. 2) has two distillation columns: the beer still and the rectifier. The fermented mash (beer) is preheated in the rectifying column and then fed to the top of the beer still along with the feints, or spent portion of the mash. The alcohol is removed in the beer still and further refined by distillation in the rectifier.

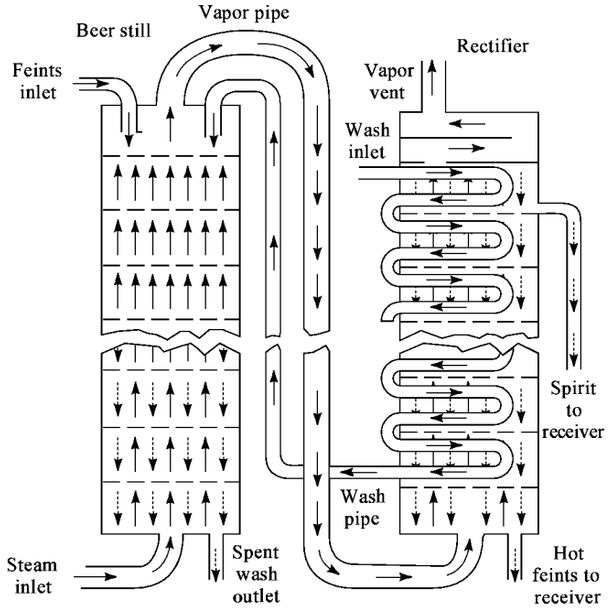

Fig. 2. Coffey continuous still.

In America, the Indians had fermented beverages made from maple syrup, corn, acorns, and other nuts. In the time of Columbus, they were drinking mezcal distilled from the fermented sap of maguey.

The colonists are said to have practiced distillation before 1650. The Virginia settlers made brandies and those in New England and the middle colonies distilled a variety of products including apple whiskey (apple jack), rum, and brandy. The first beverages made by the colonists from corn and rye were distilled on Staten Island, New York, in 1640 by William Kieft. Rum was produced in Barbados from molasses around 1650 and in colonial Massachusetts in 1657.

Distilling ingredients changed between 1790 and 1830. Rum was replaced by whiskey made from rye and corn, since molasses was becoming difficult to import. The Reverend Elijah Craig is credited with producing the first sour mash bourbon whiskey in 1789 in the area that is now Georgetown, Kentucky, located in Bourbon County and thus giving the product its name. Kentucky Bourbon was made in a manner similar to whiskey made in Scotland and Ireland except a different mash was used. It contained at least 51% corn to distinguish it from Pennsylvania rye whiskey. The mash was fermented from three to five days, distilled, and then redistilled. Even though it was known that whiskey stored in charred oak barrels becomes mellow and golden in color, most whiskey in those days was sold in its natural white state or artificially colored to resemble brandy.

In the 1880s and 1890s, whiskey production grew significantly. Excessive production and intense competition resulted in mergers such as the Whiskey Trust in Peoria and the Kentucky Distilleries and Warehouse Companies. They attempted to control production and raise prices but had little success in doing so.

Distillers distributed their whiskey in barrels. It was bottled or served in the taverns; this led to tampering and excessive dilution. In 1870 George Garvin Brown started bottling and sealing whiskey to ensure its quality. The Bottled in Bond Act of 1897 encouraged putting whiskey in bottles. It required that whiskey be bottled in bond must be 100° proof, at least four years old, and produced in one season at one distillery. The bottle was sealed with a green stamp, indicating tax payment and compliance with federal law. In 1900 the Pure Food and Drug Act was passed which required a statement of the manufacturing process and ingredients on the label. In 1909, under President Taft, whiskey was finally defined as "any volatile liquor distilled from grain." Standards of identity were developed based on current manufacturing processes for the various whiskies including bourbon and rye.

Prohibition, which made the sale of spirits illegal from 1920 to 1933, actually resulted in increased consumption from 530 to 750 million liters annually. At the end of Prohibition, many mergers occurred and modern technology was introduced to the industry.

Government Regulations and Taxation

Distilled spirits and the industry have always been subject to heavy taxation. Not only has it been an excellent source of revenue for many governments throughout the world, but high taxes can also be rationalized as having an inhibitory effect on consumption.

In England, the Magna Carta provided a standard of measurement for the sale of ale and wine. In 1643, the English Parliament proposed the first tax on distilled spirits. In the American colonies, William Kieft, Director General of New Netherland, imposed the first liquor tax of two guilders on each half vat of beer in 1640. Alexander Hamilton initiated an excise tax on domestic spirits in 1791. The tax was resented and ultimately repealed in 1800 by Thomas Jefferson. Except during the War of 1812, domestic spirits remained untaxed until 1862. At that time, a tax of $0.02 L was implemented, which has been increased periodically. In January 1991, the Federal Excise Tax on distilled spirits was raised to $3.56 per liter or $13.50 per proof gallon. In addition, many states have substantially increased the state excise taxes on distilled spirits.

In the United States, the Alcohol Tax Unit came into being with the repeal of Prohibition in 1933, and it became the Alcohol and Tobacco Tax division of the Internal Revenue Service in 1952. The Bureau of Alcohol, Tobacco, and Firearms (ATF), established in 1972, and the Department of the Treasury closely regulate the manufacture of distilled spirits.

Production and Consumption Patterns

United States distilleries produced 32 million liters (8.5 million gallons) in 1810. Production and consumption grew with the population over the next 100 years. In anticipation of Prohibition, over 1.1 billion liters (300 million gallons) of distilled spirits were produced in 1917 including 225 million liters of whiskey. Although total consumption peaked in 1981 at 1.7 billion liters, individual adult consumption peaked in 1971 at 11.6 liters per adult (Fig. 3). The decline has continued through 1990 and is projected to continue because of increasing taxes and changing attitudes and lifestyles. The consumption trend is toward lower proof, lighter alcoholic beverages covering an ever widening spectrum of products including premixed cocktails, cordials, creams, light whiskeys, and wine coolers. Although overall spirit consumption is declining, the premium segment including whiskey, vodka, and flavored products has recently shown growth, indicating a more selective, upscale consumption pattern.

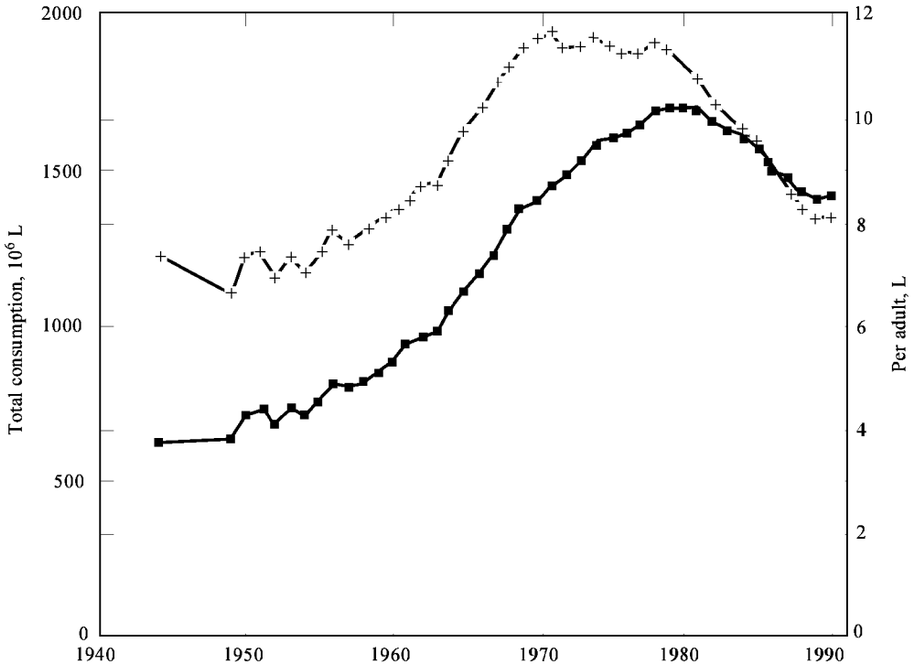

Fig. 3. Consumption of distilled spirits from 1940 to 1900, where ■, total; +, per adult (1).

Distillers' Definitions

Alcohol Yield. With corn containing 60% starch, distillers traditionally obtain 19–19.7 L (5.0–5.2 proof gallons) 0.03 m^3 (bushel). Theoretical yields as liters of absolute alcohol 100 kg of starch are

stoichiometric 72.0 L (100%)
maximum level 68.4 L (95%)
industrial standard 62–65 L (86–90%)

For the maximum level, 5% or more of carbon substrate is consumed by yeast growth and by-product formation.

Backset. Backset is the screened aqueous by-product from distillation. It is recycled and added to the cooked grain mash prior to fermentation.

Balling. Balling is a measure of the sugar concentration in a grain mash, expressed in degrees. It approximates percent by weight of the sugar in solution.

Beer. Beer is the alcoholic product arising from the yeast fermentation of saccharified grain mash. It may or may not include stillage from a previous fermentation distillation (see BEER).

Bonded Whiskey. Bonded whiskey is whiskey stored at least four years in wooden containers where the spirits have been in contact with the wood surface. It is unaltered from the original character by the addition or subtraction of any substance other than by filtration or chill proofing, is reduced in proof by the addition of water to 100° proof (50 vol %) and bottled at 100° proof, and is produced at the same distillery in the same season (January through June or July through December).

Congeners. Congeners are the flavor constituents in beverage spirits that are responsible for its flavor and aroma and that result from the fermentation, distillation, and maturation processes.

Conversion. Conversion describes the enzymatic starch hydrolysis processes, liquification, and saccharification.

Cooking. Cooking is the gelatinization by heat treatment and α-amylase liquification of raw material starch (qv).

Doubler. A doubler is a pot still used to redistill whiskey and low wines from a beer still. The low wines are fed into the doubler where they are redistilled by way of steam enclosed in a scroll at the bottom of the still. The bottoms, the organic components remaining at the bottom of the still, are returned to the beer still to extract the alcohol.

Feints. Feints are the third fraction of the distillation cycle derived from the distillation of low wines in a pot still. This scotch term is also used to describe the undesirable constituents of the wash that are removed during the distillation of grain whiskey in a continuous patent still (Coffey). These are mostly aldehydes and fusel oils.

Fermentable Sugars. Fermentable sugars like glucose *[50-99-7]*, maltose *[69-79-4]*, and maltotriose *[1109-28-0]*, can be fermented by distiller's yeast.

Foreshots. Foreshots is the first fraction of the scotch distillation cycle derived from the distillation of low wines in a pot still.

Fusel Oil. Fusel oil is an inclusive term for heavier, pungent tasting alcohols produced during fermentation. Fusel oils are composed of a mixture of *n*-propyl, isobutyl, and isoamyl alcohols.

Grain Whiskey. Grain whiskey is an alcoholic distillate from a fermented wort derived from malted and unmalted barley and corn, in varying proportions, and distilled in a continuous patent still (Coffey).

Heads. Heads is distillate containing a high percentage of low boiling components such as aldehydes.

High Wines. High wines is an all-inclusive term for beverage spirit distillates that have undergone complete distillation.

Infusion Mashing. Infusion mashing is the process of simultaneously cooking and converting small grains (rye, barley, and wheat).

Limit Dextrins. Limit dextrins are oligosaccharides containing one or more 1,6-α-linkages (see CARBOHYDRATES).

Low Wines. Low wines is the term for the initial product obtained by separating (in a pot or Coffey still) the beverage spirits and congeners from the wash. Low wines are subjected to at least one more pot still distillation to attain a greater degree of refinement in the malt whiskey.

Malt Whiskey. Malt whiskey is an alcoholic distillate made from a fermented wort derived from malted barley only and distilled in pot stills. It is the second fraction (heart of the run) of the distillation process.

Proof. The alcoholic concentration of beverage spirits is expressed in terms of proof in Canada, the United Kingdom, and the United States. U.S. regulations define this standard as follows: proof spirit shall be held to be that alcoholic liquor which contains one-half its volume of alcohol of a specific gravity of 0.7939 at 15.6°C ie, the figure for proof is always twice the percent alcohol content by volume. For example, 100° proof means 50% alcohol by volume. In the United Kingdom as well as Canada, proof spirit is such that at 10.6°C alcohol weighs exactly twelve-thirteenths of the weight of an equal bulk of distilled water. A proof of 87.7° indicates an alcohol concentration of 50%. A conversion factor of 1.142 can be used to change British proof to U.S. proof.

Wash. Wash is the liquid obtained by fermenting wort with yeast. It contains the beverage spirits and congeners developed during fermentation.

Wine Gallon. Wine gallon is the measure of actual volume; a U.S. gallon (3.785 L) contains 3785 cm^3 (231.0 cubic in.); a British (Imperial) gallon contains 4546 cm^3 (277.4 cubic in.).

Wort. Wort is the liquid drained off the mash tun containing maltose, a grain sugar derived from the conversion of starch during the mashing process by the action of the organic enzyme, maltase, found in barley malt.

Proof Gallon. Proof gallon is a U.S. gallon of proof spirits or the alcoholic equivalent thereof, ie, a U.S. gallon 3785 cm^3 (231 cubic in.) containing 50% of ethyl alcohol by volume. Thus a gallon of liquor at 120° proof is 1.2 proof gallons; a gallon at 86° proof is 0.86 proof gallons. A British and Canadian proof gallon is an imperial gallon of 4546 cm^3 (277.4 cubic in.) at 100° proof (57.1% of ethyl alcohol by volume). An imperial gallon is equivalent to 1.2 U.S. gallons. To convert British proof gallons to U.S. proof gallons, multiply by 1.37. Since excise taxes are paid on the basis of proof gallons, this term is synonymous with tax gallons.

Single Whiskey. Single whiskey is the whiskey, either grain or malt, produced by one particular distillery. Blended Scotch whiskey is not a single whiskey.

Sour Mash. Sour mash is made with a lactic culture and not less than 20% stillage added back to the fermentor and fermented for at least 72 h.

Spirits. Spirits are distilled spirits including all singular whiskeys, gin, brandy, rum, cordials, and others made by a distillation process for nonindustrial use.

Stillage. Stillage is dealcoholized fermented mash.

Tails. Tails is a residual alcoholic distillate.

Spirit Types

In spite of a decline over the past 50 years, whiskeys are still the most popular distilled alcoholic beverage group in the United States (Table 1) (1). However, vodka consumption has increased significantly to 22% of total distilled spirits in 1990.

Table 1. United States Liquor Consumption by Type, %

Type	1949	1960	1966	1978	1990
blends	66.2	31.3	24.3	10.4	5.9
straights	8.7	25.4	23.9	14.0	10.6
bonds	5.4	4.1	2.4	0.7	0.1
Scotch	4.4	8.1	10.4	12.0	8.5
Canadian	2.7	5.2	6.9	11.4	13.0
other	0.4	0.3	0.3	0.1	0.1
Total whiskey	*87.8*	*74.4*	*68.2*	*48.6*	*38.2*
gin	7.1	9.3	10.5	9.5	8.6
vodka	0.0	7.8	10.4	20.0	22.7
cordials	2.2	3.8	4.3	7.9	11.1
brandy	1.3	2.6	3.2	3.8	4.9
rum	1.3	1.6	2.2	5.8	8.3
tequila and other	0.3	0.5	1.2	4.4	6.2
Total nonwhiskey	*12.2*	*25.6*	*31.8*	*51.4*	*61.8*
Total consumption, million liters[a]	*641.5*	*888.3*	*1169.2*	*1786.1*	*1386.0*

[a] To convert liters to gallons, divide by 3.785.

Because of the economic interest in distilled spirits, each country has established standards for their various types of distilled beverages, and countries mutually respect each other's alcoholic beverage standards. U.S. Standards of Identity are given by the Bureau of Alcohol, Tobacco, and Firearms (ATF) (2).

Within each type of distilled spirits, wide variations of flavor can be achieved by the type and amount of starting grains or other fermentable materials, methods of preparation, types of yeasts, fermentation conditions, distillation process, maturation time and temperature, blending, and use of new technologies such as membrane separation.

The flavor and aroma of distilled spirits are derived primarily from minor constituents called congeners that are produced and augmented in the fermentation and maturation processes. The congener profiles for various distilled spirits are shown in Table 2.

Table 2. Congeneric Content of Various Distilled Alcoholic Beverages[a]

Component	Canadian	Scotch	Bourbon whiskey	Kentucky whiskey	Cognac brandy	Tequila
fusel oil	53.0	105.0	199.0	195.0	193.0	195.0
total acids[b]	20.0	15.0	69.0	63.0	36.0	
esters[c]	4.6	11.4	23.0	18.0	41.0	12.9
aldehydes[d]	2.0	4.1	3.9	3.2	7.6	5.3
furfural *[98-01-00]*	0.11	0.11	0.45	0.90	0.67	
total solids, g 100 mL	82.0	109.0	102.0	80.0	698.0	
tannins	18.0	8.0	52.0	48.0	25.0	21.0
color at 420 nm	5.4	5.6	9.5	8.0	11.0	

[a] Grams per 100 liters at 100° proof (50%). Determinations were made according to the official methods of analysis of the Association of Official Analytical Chemists, 15th ed., 1990.

[b] As acetic acid *[64-19-7]*.

[c] As ethyl acetate *[141-78-6]*.

[d] As acetaldehyde *[75-07-0]*.

Canadian. By government regulation, Canadian whiskeys contain no distilled spirits less than three years old. They are usually blended products and are often up to six years of age. Canadian whisky tends to be light bodied and delicate in flavor. The Canadian government sets no limitations as to mashing formulas, distilling proofs, or types of cooperage used in maturation.

As in the United States, Canadians use corn, rye, and barley malt. Their process is essentially the same as the one used by many distilleries in the United States. Since they have no limitations on distillation proofs, distillers operate their systems for optimum separation and congener concentration. In addition, they are permitted to add blenders or flavoring components up to 9.06% by volume in the final blending after the aging process.

White oak barrels of 190 liters (50 U.S. gallons) that have been previously used for bourbon maturation are often used a second and third time to age Canadian whisky. This used cooperage along with the higher proof distillation gives Canadians their characteristic light flavor compared to the heavy flavor of most bourbons aged in new charred oak barrels.

Scotch. In 1988, the Scotch Association Council approved a new, tighter definition for Scotch whisky which is as follows: "Scotch whisky is a potable spirit—

which has been produced in Scotland:

from water and malted barley, with or without whole grains of other cereals, wholly processed at the distillery into a mash, converted to a fermentable substrate solely by the indigenous enzyme systems, fermented with the addition of yeast only;
by distillation of the wash obtained there at an alcoholic strength by volume of less than 94.8% in such a way that the distillate has an aroma and flavor derived from the said materials and process; and

which has been matured in Scotland:

in oak cask of a capacity not exceeding 700 liters;
for a period of not less than three years;
in excise warehouse, which for the purpose of this definition has the meaning assigned to it by Section One of the Customs, Excise Management Act 1979; and

which retains the color, aroma, and taste resulting naturally from the above process; and
to which no substances may be added other than:

water, and
spirit caramel and

whose alcoholic strength apart from any natural evaporation losses may be reduced only by the addition of water to a bottling strength of not less than 40% alcohol by volume."

Whole grains means grains of cereals from which no part has been intentionally removed. The unique taste characteristics and smokey flavor of Scotch is developed from peat used in the whisky production process. The character and amount of peat used in malting the barley have a critical affect on the flavor intensity of the final product. The aroma of the burning peat is absorbed by the barley malt and is carried through the distillation process.

The dried malted barley is ground and mashed in a tub, after which the liquid portion is drained off, cooled, and placed in the fermentor. After fermentation, a batch distillation system is usually used to separate the whisky from the fermented wort. The still consists of a copper kettle with a spiral tube or "worm" leading from the top. The dimensions and shape of the stills have a critical effect on the character of the whisky. The product taken off in the first part of the distillation is called foreshots (heads). The middle portion is the high wines and the last portion is the feints (tails). The middle portion is redistilled at the 140–160° proof (70–80%) range and matured in used oak cooperage.

The grain whiskeys used in Scotch blends are produced using corn, rye, and barley malt and are distilled using a continuous multicolumn still at 180–186° proof (90–93%). Grain whiskeys are aged in used oak barrels of 190 liter capacities. The used barrels are often purchased in the United States from bourbon distilleries.

The single malt Scotch or malt Scotch, which has recently become popular in the United States, is made from a mash of only malted barley. Single malts are usually darker with heavier flavor than blended Scotches because of increased aging and the absence of the lighter grain whisky.

Irish Whiskey. Irish whiskeys are blends of grain and malt spirits three or more years of age that are produced in either the Republic of Ireland or Northern Ireland and comply with the respective laws regulating their manufacture. Since no peat is used in the malting process, Irish whiskey lacks the smokey character of Scotch. In the manufacturing process, the malt is soaked in water and milled to produce the wort. The fermentation usually takes about 60 hours. The first distillation in a pot still yields a 22–23% alcohol product. A second pot still distillation produces a product that is 45–46% alcohol. This is followed by a third distillation in another pot still to yield the Irish whiskey of about 68–70% alcohol.

Irish whiskey is matured in used barrels at about 63% alcohol. It is usually considered more flavorful and heavier bodied than blended Scotch whiskeys.

United States Spirits. The manufacture of distilled spirits is tightly controlled within narrow limits that are specified in reference 2. ATF regulations require that a detailed statement of the production process be submitted for approval prior to placing any process in operation.

Distilled beverages are classified according to type, materials, composition, distillation and maturation proofs, types of barrels, and maturation time.

Whiskey. Whiskey refers to any alcoholic distillate made from a fermented grain mash at less than 190° proof (95%) in such a manner that it possesses the taste, aroma, and characteristics generally attributed to whiskey. It is matured in new or used charred oak barrels. Whiskey can be further delineated by the cereal grains used and the maturation time and blending, if any.

Neutral Spirits. Neutral spirits are produced from any fermentable material and are distilled at or above 190° proof and bottled at 80° proof or higher. The substrate must be specified unless it is grain.

Grain Spirits. Grain spirits are neutral spirits from grain that are matured in used oak barrels and bottled at 80° proof or higher. The period of aging in oak may be declared on the bottle.

Vodka. Vodka is a neutral spirit made from any fermentable material and distilled in such a manner that is without any distinctive character, taste, aroma, or color. Charcoal filtration is often used in processing vodka which is bottled at 80° proof or higher. In the United States, the substrate must be specified if it is not grain. Any flavoring, if added, must be stated. The product must be bottled at not less than 70° proof and called a flavored vodka.

Light Whiskey. Light whiskey is distilled at not less than 160° proof and not more than 190° proof. It is matured in used charred-oak barrels or new uncharred barrels. Blended light whiskey is light whiskey mixed with less than 20% straight whiskey on a proof gallon basis. Distillers enjoy some latitude in the production of light whiskey matured in used barrels. As long as it is 189° proof as received in the cistern room, the distiller may do some additional blending prior to entry into the barrel.

Bourbon. Bourbon, and also rye, wheat, malt, and rye malt whiskeys, are made from a fermented mash not less than 51% corn, rye, wheat, malt, or rye malt, respectively. They are distilled at not over 160° proof and matured at not more than 125° proof in new charred oak barrels and bottled at not less than 80° proof. If stored for less than four years, it must be declared on the label.

Corn Whiskey. Corn whiskey must be distilled from a fermentable mash that contains at least 80% corn and at not over 160° proof. It is usually matured in new uncharred oak barrels or used oak barrels and bottled at not more than 125° proof.

Straight Whiskey. Straight whiskey is distilled at not over 160° proof and barreled at not more than 125° proof. It must be matured for at least two years in new charred oak barrels and bottled at not less than 80° proof. This whiskey may be called "bottled in bond" if it has been distilled at one plant, matured for at least four years, and bottled at 100° proof by the same distiller.

Sour mash fermentations must have not less than 20% stillage added back (backset) to the mash and be fermented for not less than 72 hours. A lactic culture is used and is permitted to develop for a period of not less than six hours.

Blended Whiskey. Blended whiskey is made with at least 20% of 100° proof straight whiskey either separately or in combination with whiskey or grain neutral spirits. When a blended whiskey contains at least 51% (v v) of straight whiskey (eg, bourbon), it may be labeled as blended bourbon or bourbon whiskey, a blend.

Tennessee Whiskey. Tennessee whiskey is a product made by Tennessee distillers and processed in a manner similar to bourbon. However, Tennessee whiskey is filtered through maple charcoal prior to maturing which gives it its distinctive flavor. Tennessee distillers make their own charcoal by slowly burning 1.8-m lengths of hard maple wood. During the burning process the wood is periodically wet down to cause it to char rather than

disintegrate into ashes. The charcoal is pulverized and packed into tanks and the new whiskey is allowed to filter through the charcoal. This adds an extra smoothness character to the whiskey.

Gin. Gin is a botanical flavored spirit first produced in 1650 by Franciscus de La Boe, a professor of medicine at the University of Leyden, attempting to produce a palatable, therapeutic medicine. He distilled alcohol in the presence of juniper berries being aware that the Latin juniperus communis means youth giving.

Gins derive their character from the type of mash used to produce the grain neutral spirits and the quality of the juniper berries and other botanicals used in the redistillation process. A wide variety of botanicals is used in gin including angelical root, anise, carroway seeds, citrus peels, licorice, and other barks, herbs, and roots.

U.S. regulations define two types of gin; distilled gin and compounded gin. Distilled gin is produced from the original mash or the redistillation of neutral spirits with juniper berries and other botanicals. Distilled gin may retain this labeling as long as juniper berries are present during distillation and other aromatics used in the formula may be added as liquid concentrates purchased or produced by the distiller.

Compounded gin is produced by adding extracts of juniper berries and other botanicals to high proof neutral spirits. This gin is perceived to be a lower quality than distilled gin and not much is produced by this method.

Gin is usually distilled at 180–190° proof. In the second distillation, crushed juniper berries are placed on mesh trays or perforated racks called gin heads in the distillation column. The vapors then extract the aromatic flavoring oils and carry them over with the distillate.

London dry gin is produced from a mash containing more barley and less corn, which is said to give the product more smoothness. This gin is distilled at high proof often under reduced pressure at about 57°C to avoid thermal decomposition and enhance smoothness.

Other Types of Spirits.

Brandy. Brandy is a distillate from fermented juice, mash, fruit wine, or fruit residues. It is distilled at less than 190° proof in such a manner as to produce the taste, aroma, and characteristics generally attributed to brandy. Fruit brandy is distilled solely from the fermented juice or mash of whole, ripe fruit or from standard grape, citrus, or other fruit wine. Brandy distilled exclusively from one variety of fruit must be so designated, except grape brandy which can be identified by the term brandy. Brandy must be matured a minimum of two years in oak barrels, otherwise it must be labeled immature.

Brandies are distilled using batch or continuous systems. Variations of the pot still are used in France. Elsewhere, both systems are used. The batch system yields a more flavorful product, whereas the continuous still yields a lighter flavor. The first distillate using a pot still is taken off at 60° proof. It is then redistilled to 148–160° proof. Brandy is matured in charred-oak barrels for two to eight years and bottled at 80° proof or higher.

The most famous brandy comes from the Cognac region of France. It is double distilled in traditional pot stills by small farmers and sold to the blenders for aging in limousin oak casks. French law requires that the stills be 3000 liters or less and that the distillation be completed by March 31.

Armagnac, another well-known French brandy produced since 1422, must originate from the Armagnac district of France to be so labeled. It is described as fuller, richer, and more mellow than Cognac. Armagnac is produced from wines using continuous copper stills and aged in 400-L oak casks with ridged staves to expose more of the surface area.

In the United States about 95% of the brandy comes from California. The first brandy was made in 1837 though it was not produced in quantity until 1867. All California brandy must be made from grapes grown and distilled in the state and aged a minimum of two years in oak barrels.

Rum. Rum is a distillate from the fermented juice of sugar cane, sugar cane syrup, molasses, sugar beets, or other by-products distilled at less than 190° proof in such a manner that it possesses the taste, aroma, and characteristics generally attributed to rum. It is bottled at not less than 80° proof.

There are three types of rum: light or amber, full-bodied, and aromatic rums. Light rum is also called white rum and is usually colorless having a very light molasses flavor. It is distilled on a multicolumn continuous still at 160–180° proof and can be matured in either glass, stainless steel, or uncharred oak barrels. The age of the rum does not need to be declared on the labels. Light-bodied rums are distilled in Puerto Rico, the Virgin Islands, Cuba, the Dominican Republic, and Haiti.

Amber or gold rums can be matured in wood barrels three years, though the color in gold rums should not necessarily imply that it was derived from aging. Often the color is achieved by adding caramel color to the product. They are more flavorful than light rum.

Full-bodied rums are allowed to ferment from 12 to 20 days, often relying on natural or wild fermentation in which the mash is inoculated by the yeast present in the air and starting materials. These rums are twice-distilled in pot stills to 140–160° proof. Full-bodied rums are often aged from five to seven years in oak barrels. Caramel color can also be added to give them a darker color. They are produced in Jamaica, Barbados, Martinique, Trinidad, and Guyana.

Aromatic rum is produced on the Island of Java in Indonesia. It derives its unique aromatic character from the addition of dried red Javanese rice cakes to the fermenting mash. After maturating for three to four years, the rum is shipped to Holland for additional aging prior to blending and bottling.

Tequila. Tequila is an alcoholic distillate produced in Mexico from the fermented juice of the heads of the Agave Tequilana Weber (blue variety) cactus. It is cultivated and takes 8 to 12 years to mature. Only the heart or the head of the plant, which weighs 36–50 kg, is used. It is chopped and steamed in a masonry oven for 9 to 24 hours depending on the rate at which inulin is converted to fermentable sugars. After a 12-h cooling period, the cooked heads are shredded and rolled to separate the juice from the pulp. The pulp residue is washed with water to remove additional sugars. Both the juice and pulp washings are then pumped into 3800–7500-L fermentors. The juice and pulp wash can be supplemented with sugar cane syrup or brown sugar not to exceed 50% of the total fermentable sugar. Ammonium sulfate can be used as a nutrient for fermentation. Water is added to the fermentable mixture so that the sugar content is about 9% (w/v). The fermentation takes 38 to 42 hours at a temperature of about 36°C. The final alcohol concentration is about 4.5% (w/v).

The fermented mash is pumped into a 1100-L copper pot still. The primary distillate is collected at 28° proof. It is redistilled in a larger pot still at 110° proof. The residual distillate is combined with fermented mash to start a new cycle in the first distillation.

Tequila is usually bottled at 80–86° proof. It is sold unaged as white tequila or it can be matured in oak barrels. Aging gives Tequila a golden color and a pleasant mellowness without altering its basic taste.

Tequila can only be produced in an area of Mexico known as Tequila in the state of Jalisco, about 40 miles from Guadalajara. It is called mezcal or maguey when produced outside of Tequila.

Cordials and Liqueurs. Cordials and liqueurs are the same products, with the different names being the American and European designations, respectively. They are produced by blending or redistilling neutral spirits, brandy, or other distilled spirits, with fruits, flowers, plants, juices, or concentrates, and other natural flavoring materials or extracts derived from infusions, percolations, or macerations of such materials. Cordials must contain a minimum of 2.5% (w/w) of sugar or dextrose or a combination of both. If the added sugar and dextrose are less than 10% (w/w), the cordial may be designated as dry. Most cordials contain larger amounts of sugar and other sweeteners. U.S. cordials containing synthetic or artificial flavoring materials must be labeled and are considered a spirits specialty.

A tremendous variety of cordials are available in a wide spectrum of flavors from fruits, peels, leaves, roots, herbs, seeds, and barks. The proofs range from 25° to 100°.

Cordials were said to be produced in ancient Egypt and Athens. Commercial production started in the Middle Ages when alchemists, physicians, and monks were searching for the "elixir of life." Many well-known cordials were developed in this period, such as Benedictine and Chartreuse, both bearing the names of the monasteries where they were first developed.

Benedictine was made in 1510 by Dom Bernardo Vincelli at the abbey in Frecomp, Normandy. It is one of the few liqueurs that is aged for four years after blending. Benedictine and Brandy (B&B) was introduced in 1937 after the discovery that Americans were adding brandy to Benedictine. Chartreuse, first made in 1605, is formulated with over 130 herbs and spices macerated in brandy.

Manufacturing Process

Ethyl alcohol *[64-17-5]*, C_2H_6O, is produced by the fermentation of materials containing sugar or substances convertible to sugar, such as starches and fruit processing residues. Cereal grains are usually used in the production of beverage distilled spirits. Beverage alcohol is always ethyl alcohol, CH_3CH_2OH.

Higher alcohols may be present in distilled spirits and are referred to as fusel oils or by specific name.

Composition of grains varies considerably and depends on factors such as climate, soil, and hybrid variety. Another variable is the malt; it is generally germinated barley, though rye malt or wheat malt can be used. The malting process develops the active enzymes (amylases) in the grain that convert grain starch into dextrins and then to maltose, a fermentable sugar. The malt and malting technique also can affect the final flavor and aroma of the alcohol, as in the case of Scotch whisky.

Grain Handling and Milling. The beverage industry utilizes premium cereal grains with particular specifications, especially in regard to the elimination of grain with objectionable odors which may have developed during storage or drying at the elevators. Hybrid corn, usually of the yellow dent variety, along with rye, barley, and wheat (small grains), is used for beverage alcohol production. The corn usually contains 60% starch and 12–14% moisture. U.S. No. 2 grade or better corn is used in the distilling industry. The small grains are selected for the unique flavors they add to distillates.

Distilleries receive grain in either hopper railcars or trucks. It is usually transferred from the unloading pit by a pneumatic conveyor system or auger system. Even though the grain has been subjected to a cleaning process at the elevator, it is passed over receiving separators, a series of vibrating screens that sift out foreign materials. Air jets and dust collectors remove light materials and magnetic separators remove items containing iron.

Milling breaks the outer cellulose protective wall around the kernel and exposes the starch to the cooking and conversion processes. Distillers require an even grind with as small a particle size as can be physically handled by the facility.

Milling is usually accomplished by two methods. Hammer mills use a series of revolving hammers within a close-fitting casing, rotating at 1800–3600 rpm to shear the grain to a meal that is removed by suction through a screen with different meshes for various types of grain. Cage mills use a series of counter rotating bars at high speed to grind the grain by impact. The grind is, however, not as uniform as hammer mills and produces much more flour.

Mashing. The mashing process consists of cooking (gelatinization) the starch and converting (saccharification) it to grain sugar (maltose). Cooking can be carried out at or above atmospheric pressure in either a batch or continuous system. For whiskey production, batch cooking at atmospheric pressure is widely used, although some batch pressure cooking is practiced. For grain neutral spirits production, both batch and continuous systems are used under pressure. After cooling, conversion is accomplished in the cooking vessel by adding barley malt or enzymes from other sources to the cooked grain. Some distillers immediately pump the mash to a converter for the necessary holding time and thus make the cooking vessel available for the next cook. The converted mash is cooled and pumped to the fermentors.

Some bourbon distillers use gibberellin-treated malt along with glucoamylase to reduce by 50% the amount of malt in their grain bills and thereby lower production costs.

Distillers vary mashing procedures, but generally conform to basic principles, especially in the maintenance of sanitary conditions. The cooking and conversion equipment is provided with direct or indirect steam, propeller agitation, and cooling coils.

Rye. In the preparation of a bourbon mash, rye is not always subjected to the corn cooking process. However, rye undergoes liquefaction at a much lower temperature than corn. This avoids thermal decomposition of critical grain constituents adversely affecting the final flavor of the distillate. Rye is often mashed separately.

Corn. Although the starch in corn converts easily, higher cooking temperatures are needed to make the starch available. Usually malt is not added at the beginning; one-half percent premalt may be added before cooking, preferably at around 66°C, to reduce viscosity. Thin stillage (residual dealcoholized fermented mash from the distillation process) is added by some producers to adjust pH to 5.2–5.4. For cookers operating at atmospheric pressure, a mashing ratio of 95–115 L (25–30 gal) of slurry (grain, water, and stillage mixture) per 0.03 m^3 (1 bushel) and a holding time of 30 min at 100°C is preferable. The mash is cooled to 67°C and malt is added.

Conversion. Primary conversion refers to the saccharification taking place during conversion and is in the order of 75–85% of the available starches. The remainder of the conversion to fermentable sugar takes place during the fermentation process and is referred to as secondary conversion. For batch cooking under pressure, only 83–99 L (22–26 gal) of water bushel are drawn, and the maximum temperature is 120–152°C. In continuous pressure cooking, water is drawn at a ratio of 30 L m^3 (24 gal bu) of meal and sufficient thin stillage is added to adjust the pH to 5.2–5.4. The mash is pumped through the continuous pressure cooker, where it is exposed to temperatures of 170–177°C for 2–6 minutes, and then into a flash chamber, where it is cooled immediately to the malting (conversion) temperature of 63°C. A malt slurry is continuously introduced and the mixture proceeds through the water cooling system to the fermentors.

Particle size and cooking condition for the grain slurry vary depending on the type of distilled spirit that is to be produced. In the case of corn grain fermentations, distillers use small size, high temperature, and low beer gallonage (higher starch concentrations) for neutral spirits production at 120–170°C and 76–91 L 0.03 m^3. Bourbon distillates call for low temperatures (100–150°C) and thinner mash of 95–115 L 0.03 m^3 (saccharified starch slurries) out of flavor considerations. (0.03 m^3 is approximately a bushel).

Saccharification enzymes shorten (liquefy) the cooked starch paste by randomly hydrolyzing α-1,4 linkages. α-Amylase *[9000-85-5]* enzymes are the principal catalysts of this activity. β-Amylase *[9000-91-3]* successively forms two unit maltose sugar from the starch chain pieces. α-1,6 Linkages within the starch molecules are cleaved by limit dextrineases from malt; glucoamylase of fungal origin can hydrolyze both α-1,4 and 1,6 linkages, splitting off one unit of glucose sugar. In all cases, the 1,6 breakdown proceeds slower than 1,4 breakdown.

The catalytic activities of enzymes are optimized within pH values of 4.8–5.2. Temperatures of 60–65°C are commonly employed to secure good conversion, prior to addition of yeast.

Fermentation. The saccharified grain mash is cooled to around 20°C prior to setting the fermentor and inoculation with yeast. It is general practice to dilute the hot grain mash to its final solids concentration by adding backset stillage or water. Stillage is screened dealcoholized fermented grain beer, taken from the bottom of the alcohol distillation beer still. The use of backset stillage offers the distiller water conservation, nutrient supplements, pH adjustment of the fermentation, and a medium that inhibits the formation of by-products, such as glycerol.

Selected yeast strains of *Saccharomyces cerevisiae* are used to inoculate the mash. Two to four percent (v v) is a minimum for bourbon, which represents over four million cells per milliliter of mash. During fermentation the cells grow in number via budding and the final counts are increased a minimum of 100-fold.

Yeast (qv) metabolize maltose and glucose sugars via the Embden-Meyerhof pathway to pyruvate, and via acetaldehyde to ethanol. All distillers' yeast strains can be expected to produce 6% (v v) ethanol from a mash containing 11% (w v) starch. Ethanol concentration up to 18% can be tolerated by some yeasts. Secondary products (congeners) arise during fermentation and are retained in the distillation of whiskey. These include aldehydes, esters, and higher alcohols (fusel oils). Naturally occurring lactic acid bacteria may simultaneously ferment within the mash and contribute to the whiskey flavor profile.

A typical bourbon fermentation continues for 72 hours at a fermentation temperature within the 31–35°C range. Many fermentation vessels are equipped with agitation and or cooling coils that facilitate temperature control. Significant increases in yeast numbers occur during the first 30 hours of fermentation. Over 75% of the carbohydrate is consumed and converted to ethanol. Within 48 hours, 95% or more of the ethanol production is complete.

The finished beer (final grain residue alcohol mixture) is ultimately agitated to resuspend its solids, and transferred to the beer well storage vessel for holding until it is pumped to the beer still. Distillers try to minimize aeration at this point to avoid formation of excessive aldehydes.

From the beer well, the residue–alcohol suspension passes through a preheater where it is warmed by heat transfer from the vapors leaving the still. The preheated beer is then ready for distillation. The condensate from the preheater is returned to the beer still.

German Mashing Process. In this process, less water is used during the cooking and conversion procedure. A mashing ratio of 84 L of water per 0.03 m^3 of grain mash is used. As the heat of fermentation builds up, cold water is added to maintain the desired fermentation temperature of 31–32°C. The water is added at intervals to the fermentor until the final beer gallonage is reached for distillation in the approximate range of 133 L per 0.03 m^3. The amount of added water will depend on the individual distiller and the initial set temperature of the fermentor.

This system has many advantages. It can produce distillates of different flavors. The process conserves energy in the cooking operation because there is less water to heat and less cooling required to lower the mash to conversion temperature. Water conservation means less pumping and lower sewer discharge volumes. The process yields increased capacity of the plant at the mashing stages as well as fewer capital requirements for heat exchangers.

The converted mash is pumped to a clean sterilized fermentor and the yeast inoculum is added. The set temperature range for whiskey fermentation of 72 hours is usually 17–21°C. At the beginning, the mash converted composition is approximately 80% sugars, mainly maltose and some (<1%) dextrose (primary conversion). The pH is adjusted to reduce initial bacterial growth. Grain neutral spirits are usually set at 27–29°C to expedite fermentation. Temperatures above 35°C inhibit yeast reproduction and promote rapid bacterial growth. Above 40°C actual yeast kill occurs.

After 30 hours, the maximum and critical fermentation is underway and the pH must remain above 4.0 for optimal fermentation. However, accompanying bacterial contamination from various sources such as yeast contamination, improper cleaning procedures, slow yeast growth, or excessive temperatures can result in a pH below 4.0. The remaining amylase enzymes, referred to as secondary conversion agents, are inactivated and can no longer convert the dextrins to maltose. Under these circumstances, the fermentor pH continues to drop because of acid production of the bacteria, and the pH can drop to as low as 3.0. The obvious result is a low ethanol yield and quality deterioration.

Distillation. Distillation separates and concentrates the alcoholic products of yeast fermentation from the fermented grain mash (3). In addition to the alcohol and the desirable congeners, the fermented mash contains solid grain particles, yeast cells, water-soluble proteins, mineral salts, lactic acid, fatty acids, and traces of glycerol and succinic acid. Although a great number of different distillation processes are available, the most common systems used in the United States include: the continuous whiskey separating column (beer still), with or without an auxiliary doubler unit for the production of straight whiskeys; the continuous multicolumn system used for the production of grain neutral spirits; and the batch rectifying column and kettle unit, used primarily in the production of grain neutral spirits that are subsequently stored in barrels for maturation purposes. In the batch and extractive distillation systems, the head and tail fractions are separated from the product resulting from the middle portion of the distillation cycle.

Absorptive distillation, involving the addition of water to the upper section of a column in the whiskey distillation system, is a method of controlling the level of heavier components in a product.

In the beverage distillation industry, stills and auxiliary piping are generally fabricated of copper, although stainless steel is also used. All piping that conveys finished products is tin lined copper, stainless steel, or glass.

Whiskey Distillation. The whiskey column consists of a cylindrical shell divided into three sections: stripping, entrainment removal, and rectifying. The stripping section contains from 14 to 21 perforated plates, spaced 56–61 cm apart. The sieve holes are usually 1–1.25 cm in diameter and take up about 7–10% of the plate area. The vapors from the bottom of the still pass through the perforations with a velocity of 6–12 m s. The fermented mash is introduced at the top of the stripping section and then passes from plate to plate through descending pipes until it reaches the base where the residual mash is discharged.

Whiskey stills are usually fitted with entrainment removal sections that consist of a plate above the top stripping plate to remove particles trapped in the vapor.

The rectifying section contains three or four bubble cap (wine) plates in the top section of the still to produce distillates up to 160° proof. Whiskey stills are usually made of copper, especially in the rectifying section, which often yields a superior product. Additional copper surface in the upper section of the column may be provided by a demister, a flat disk of copper mesh. Stainless steel is also used in some stills.

Steam is introduced at the base of the whiskey column through a sparger. Where economy is an important factor, as in a fuel alcohol plant, a calandria is employed as the source of indirect heat. The diameter of the still, number of perforated and bubble cap plates, capacity of the doubler, and proof of distillation are the critical factors that largely determine the characteristics of a whiskey.

Bourbon Distillation. The basic distillation system for the production of bourbon and other straight whiskeys consists of a beer still and a beer heater, thumper, or doubler (Fig. 4). The whiskey still consists of between 14 and 21 stripping trays. The upper portion of the still is fitted with either a bubble cap section or a section packed with copper rings to enhance the removal of unwanted flavors and ethyl carbamate precursors. The reduction of carbamate precursors requires strict adherence to a cleaning protocol with a 5% caustic solution as often as twice a week.

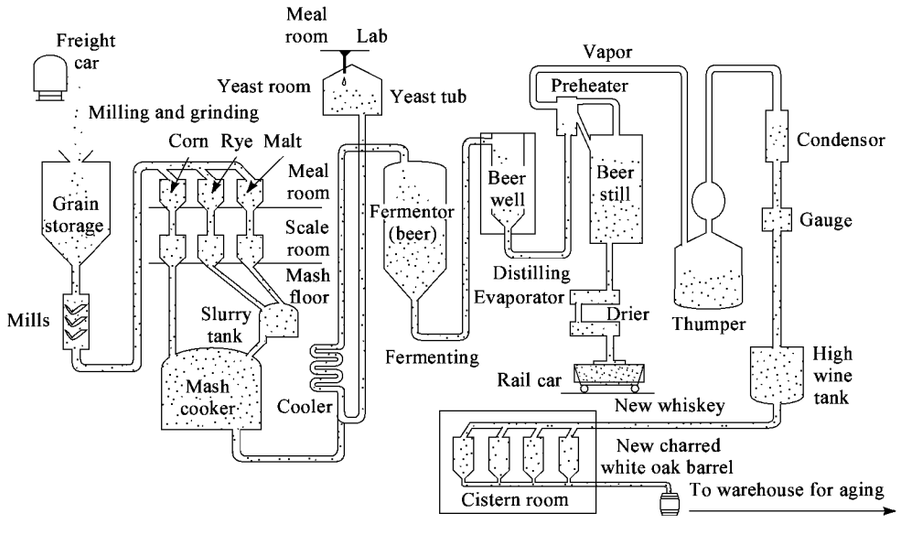

Fig. 4. Distilled beverage plant process flow sheet.

Grain Neutral Spirits Distillation. The distillation system for the production of grain neutral spirits usually consists of a whiskey separating column, an aldehyde column (selective distillation column), a product concentrating column (alcohol or rectifying column) from which the product is drawn, and a fusel oil concentrating column. In addition, some distillers may include an aldehyde concentrating column (heads concentrating column), or a fusel oil stripping column.

A fermented mash (generally 90% corn and 1–5% barley malt) with an alcohol concentration of approximately 7% (v v) is pumped into the whiskey column for stripping somewhere between the thirteenth and nineteenth perforated plate. The spent beer is discharged at the base and pumped to the feed recovery plant where it is separated into stillage (backset) and by-products. The overhead distillate, ranging in proof from 105° to 135°, is fed to the selective distillation column (aldehyde column), which has over 75 bubble cap plates. The main stream (10–20° proof) from the selective distillation column is pumped to the product concentrating column. A heads draw (aldehydes and esters) from the condenser is pumped to the heads (aldehyde) concentrating column, and a fusel oil and ester draw is pumped to the fusel oil concentrating column. The product is withdrawn from the product concentrating column.

By-Products. After the removal of alcohol, the fermentation residues are processed to produce distillers grains. These residues consist of proteins, fats, minerals, vitamins, and fiber that are concentrated threefold by removal of the starch. Distillers grains are usually divided into one of four groups including distillers dry grains (DDG), distillers dry solubles (DDS), distillers dry grains with solubles (DDG S), and condensed distillers solubles (CDS).

Distillers grains are often classified as light or dark. Processing the whole stillage (5–8% solids) yields DDG S (dark grains). The light fraction results from screening out the coarse material to yield thin stillage which is concentrated by centrifugation and or evaporation to give the CDS. DDS are produced by spray or drum drying the CDS.

Typical composition for corn DDG S is 26–28% protein, 14–20% fat, 11–16% fiber, and 6–9% moisture; for DDS it is 25–30% protein, 15–20%

fat, 5–8% fiber, and 5–9% moisture.

The annual production of DDG is over one million tons. Most of it is used in animal feed. However, increasing quantities are being sold as food ingredients because of its excellent nutrient and fiber content.

Maturation

The oak barrels used for aging distilled spirits play a significant role in determining the final aroma and flavor of the beverage. Newly distilled whiskey is colorless, grainy, and harsh. The new whiskey undergoes many types of physical and chemical changes in the maturation process that smooth it out and give it character. These changes include extraction of the wood compounds, decomposition and diffusion of the wood macromolecules into the alcohol, reactions of the wood and distillate components with each other, and diffusion through the wood and evaporation of components.

Much work has been reported and summarized in the literature on the maturing of various whiskeys in charred or uncharred white-oak barrels (4–7). The early literature indicates that total acids, aldehydes, esters, solids, and color increased with aging time and that their concentrations were inversely proportional to proof. Thus aging at higher proofs (over 127°) yields less color and flavor. The maximum allowable entry proof for straight whiskeys was increased from 110° to 125° by the U.S. Treasury Department in 1962.

It has been shown that aromatic aldehydes including vanillin, syringaldehyde, coniferaldehyde, sinapaldehyde, and ethyl lignin come from charred wood, the length of maturing directly affects the amount of aldehydes formed, the lower proof spirits have more aldehydes than higher proof spirits do, and the used and new uncharred barrels produce about one-third of the aromatic aldehydes found in new charred barrels (Table 3) (8).

Table 3. Concentration of Aromatic Aldehydes in Bourbon as Influenced by Barrel Treatment, Age, and Proof

Barrel treatment	Age, yr	Proof[a]	Concentration, g 100 L at 100 proof[a]
reused	3.5	136.6	0.33
	6.0	137.0	0.27
new charred	4.0	107.6	0.88
	1.5	140.8	0.77
	6.0	136.7	0.29
reused, recharred	3.5	136.0	0.48

[a] 100 proof 50 vol% alcohol.

It has also been proposed that under the acidic conditions found in whiskeys, ethanol reacts with lignin (qv) to reduce an alcohol-soluble form of lignin (ethanol lignin). This can be converted into coniferyl alcohol, which can be oxidized to coniferaldehyde. The partial oxidation of ethanol lignin can produce sinapic and coniferyl alcohols that can be converted to syringaldehyde and vanillin, respectively (8).

Age versus congener development in bourbon stored for eight years has been studied (9). Results indicate a high correlation of congener formation with age (Table 4).

Table 4. Statistical Analysis of Age Versus Congener Formation in Bourbon

Property Substance	Correlation coefficient[a]
total acids	0.699
esters	0.751
fusel oil	0.378
aldehydes	0.679
total color	0.686
organic-soluble color	0.672
solids	0.750
ethyl acetate	0.679
n-propyl alcohol	0.188
isobutyl alcohol	0.276
isoamyl alcohol	0.403
sodium	0.054
potassium	0.662
calcium	0.484
magnesium	0.102

[a] Correlation coefficients above 0.403 are significant.

It has been found that the cloudiness in whiskey could be caused by certain steroids extracted from the wood during aging. These include β-sitosterol-D-glucoside, β-sitosterol, stigmasterol, and campesterol (10). The monosaccharide composition of whiskey aged up to 12 years also has been followed. Arabinose, glucose, xylose, rhamnose, and galactose increased throughout the 12 years of aging while fructose increased linearly for six to seven years. This indicates that the sugars found in aged whiskey are derived from the free sugars in the wood and or the hydrolysis of hemicellulose (qv).

A study of the effect on the congener levels of up to eight refills of a used whiskey barrel indicate that volatile acids, esters, colors, solids, and tannins showed the greatest percentage change between the first and second use of a new charred barrel (11).

The amounts of color, solids, fixed acids, and tannins found in whiskey aged for two years were found to be greater in recharred barrels than in new barrels reused once. Both these levels were less than the amounts found in new charred barrels, indicating that some congener precursors are depleted as the barrels are reused and or recharred. The same study indicates that congeners increased with storage temperature. The principal congeners increased between 2% and 3% per degree centigrade over a range of 18–23°C.

The lignin and tannin contents of oak that had been in contact with both whiskey and air also has been studied (12). The lignin and tannin contents were 7 to 26 times lower at the whiskey surface versus the air surface. The aromatic aldehyde content was 8–15 times greater at the whiskey surface. New barrels contributed over two times more lignins and tannin to whiskey than the used barrels. Aldehydes were four times greater in whiskey aged in new barrels versus used barrels. When two 15-year-old whiskeys were analyzed, one characterized as light and the other heavy and flavorful (Table 5), the compounds derived from wood were significantly higher in the more flavorful whiskey, demonstrating the important contribution that wood makes to the flavor of whiskey.

Table 5. Concentration, mg/L, of Wood Components in Light and Heavy 15-Year-Old Whiskey

Property	Light	Heavy
tannins	192.0	540.0
lignin complex	515.0	1431.0
vanillin *[121-33-5]*	4.3	13.6
syringaldehyde *[134-96-3]*	8.7	29.9
coniferaldehyde *[458-36-6]*	0.8	5.7
sinapaldehyde *[4206-58-0]*	0.78	3.5
total aldehydes	14.58	52.7

Alcohol Reduction

Pervaporation. Vapor arbitrated pervaporation is used to remove ethanol from whiskey by selective passage of the alcohol through a membrane. Whiskey flows on one side of a membrane. A water-vapor stream flows on the other side and sweeps away the ethanol that permeates the membrane. Thus alcohol reduction and selective retention of flavor and aroma components can be achieved using membranes with a particular porosity. The ethanol can be recovered by condensing or scrubbing the vapor stream. Pervaporation systems operate at or slightly above atmospheric pressure (Fig. 5).

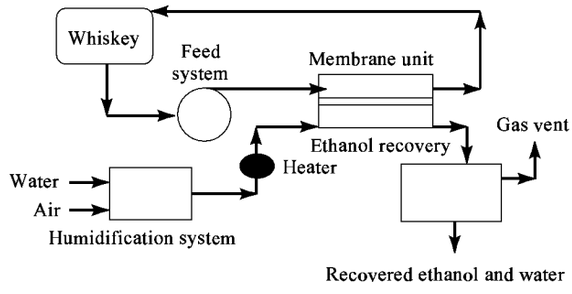

Fig. 5. Alcohol reduction pervaporation system.

In this process the addition of water vapor to the sweep stream can be controlled so that the water activity of the gas phase equals that of the beverage. When this occurs, there is no transport of water across the membrane. The water content of both the beverage feed and the sweep stream is kept constant. These conditions must be maintained for optimum alcohol reduction. The pervaporation system controls the feed, membrane, airstream moisture level, and ethanol recovery functions. An operational system has been developed (13).

The feed system handles the storage, circulation, and temperature control of the whiskey. Since permeability increases with temperature, and considering the heat stability of whiskeys, it is desirable to operate the system above ambient temperatures. Operating at higher temperatures facilitates temperature control of the process, since heat losses can be compensated by the addition of heat.

The membrane system consists of multiple plate and frame stacks holding the thin-film composite membranes clamped together. The system capacity is increased by increasing the number of plates.

A humidification subsystem controls the temperature, flow rate, and relative humidity of the sweep stream. Air and water can be fed to a liquid-gas packed contactor to produce the desired moisture level in the vapor stream. The saturation temperature controls the water loading of the air which can be heated to give exactly the desired relative humidity.

Ethanol removed by the vapor stream can be recovered by condensation, vapor recompression, or scrubbing. In the first two methods, the concentration of the recovered ethanol depends on the relative humidity of the sweep stream and the ratio of sweep and permeation rates. In scrubbing, the rate of water delivery to the liquid-gas contactor affects the ethanol concentration in the recovered stream.

Pervaporation has been successfully used both to reduce the alcohol content and to concentrate the congeners in bourbon whiskey (Table 6). The resulting products had taste, aroma, and color characteristics similar to the original bourbon but at a substantially higher intensity, reflecting the effect of the alcohol reduction and congener concentration.

Table 6. Alcohol Reduction Using Pervaporation Process

	Example 1	Example 2
initial whiskey volume, mL	1160.0	1410.0
initial alcohol concentration, %	65.3	59.7
final whiskey volume, mL	670.0	940.0
final alcohol concentration, %	41.9	38.8
processing time, h	2.6	3.1
whiskey temperature, °C	30.0	30.0
whisky flow rate, mL/min	500.0	420.0
sweep air temperature, °C	30.0	30.0
sweep air flow rate, L/min	22.5	22.5
relative humidity of sweep airstream, %	77 ± 2	80 ± 2
ethanol flux, 10^{-3} mL/(cm^2·h)	92.0	77.0
water flux, 10^{-3} mL/(cm^2·h)	6.9	2.4
ethanol concentration in condensed permeate, %	80.0	79.9

Reverse Osmosis. A reverse osmosis (RO) process has been developed to remove alcohol from distilled spirits without affecting the sensory properties (14). It consists of passing barrel-strength whiskey through a permeable membrane at high pressure, causing the alcohol to permeate the membrane and concentrating the flavor components in the retentate.

The one-pass system consists of a feed tank, filter, pump, and membrane system (Fig. 6). The feed tank contains whiskey at approximately 100° proof. It is filtered through a cellulose filter and then pumped into the membrane system where the separation takes place. Dupont B-10 Aramid hollow fiber membranes are used in series or parallel and are able to withstand the high pressures, 689–1034 kPa (6.8–10 atm), necessary to achieve separation.

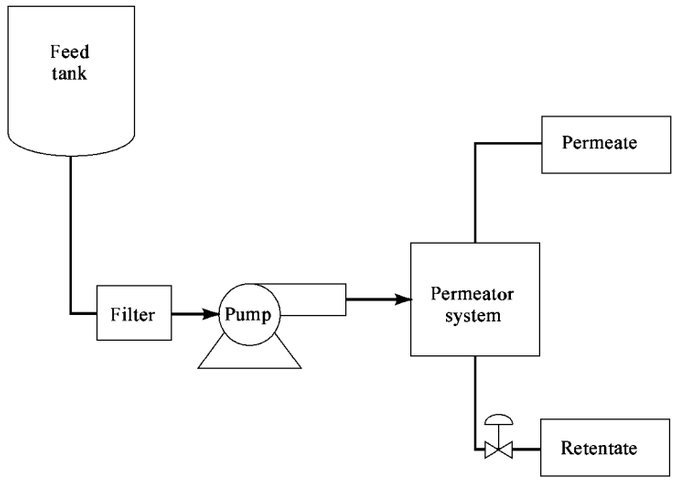

Fig. 6. High pressure reverse osmosis system for alcohol reduction.

Operational temperatures of 4–27°C are maintained. In this process the flavor components are concentrated in the retentate. A reduced alcohol product is obtained by adding back water to give the desired flavor impact. Typical gas chromatographic results, comparing unprocessed 80° proof whiskey with reverse osmosis processed 54° proof whiskey and diluted 54° proof whiskey, indicate good congener retention in the alcohol-reduced (RO) processed whiskey (Table 7).

Table 7. Congener Concentrations, mg/100 mL, of Unprocessed, RO Processed, and Water Diluted Whiskeys

Congener	CAS Registry Number	Whiskey sample		
		Unprocessed[a]	RO processed[b]	Water diluted[b]
acetaldehyde	*[75-07-0]*	1.08	1.08	0.72
methanol	*[67-56-1]*	2.48	1.59	1.65
ethyl acetate	*[141-78-6]*	8.76	8.45	5.84
n-propanol	*[71-23-8]*	2.88	2.84	1.92
isobutyl alcohol	*[78-83-1]*	7.00	6.91	4.67
n-butanol	*[71-36-3]*	0.04	0.05	0.03
ethyl proprionate	*[105-37-3]*	0.20	0.19	0.13
acetal	*[1820-50-4]*	0.72	0.32	0.48
isoamyl alcohol	*[123-51-3]*	15.44	15.09	10.29
amyl alcohol	*[71-41-0]*	6.16	5.99	4.11
isoamyl acetate	*[123-92-2]*	0.037	0.036	0.024

[a] 80 proof 40 vol%.

[b] 54 proof 27 vol%.

Seagrams has used this process to produce Mount Royal Light and V. O. Light, both 54° proof, full-flavored products that are currently in test markets in the United States and Canada, respectively.

Analytical Procedures

Analytical results of distilled spirits are expressed either by chemical class or by individual constituent. When these results are expressed by chemical class, the most prevalent constituent within that class is used as the marker, eg, acetic acid for acids, acetaldehyde for aldehydes, and ethyl acetate for esters. Wet chemical methods are employed in the determination of results by chemical class, while more advanced and refined techniques are employed in the determination of individual chemical constituents.

Alcoholic beverages are made up primarily of ethanol, congeners, and water. Congeners are vaporized with the alcohol in distillation below 190° proof and are developed during the maturation process by oxidation and other reactions. These components contribute to palatability and create the characteristic appearance, aroma, and taste of a particular spirit. When the spirit is distilled at a lower proof, more congeners are present and the spirits possess more character. Congeners are usually reported either as grams per 100 liters at "as is" proof, or as 100° proof at parts per million or parts per billion.

Distilled spirits are governed by the Bureau of Alcohol, Tobacco, and Firearms regulations. Every bottle of distilled spirits must contain a specified percent of alcohol or proof as stated on the label. Proof is the ethyl alcohol content of a liquid at 15.6°C, stated as twice the percent of ethyl alcohol by volume.

The proof content is determined by the use of a standardized hydrometer with a standardized thermometer. The alcohol content can also be determined by the use of an immersion refractometer, a pycnometer, or a density meter.

In order to determine the true proof of a distilled spirit sample, it must not contain solids. However, if the sample contains less than 600 mg 100 mL of solids, an obscuration factor can be used; it is added to the apparent proof. For example, one hundred milligrams of solids per 100 milliliters reduces the apparent proof by 0.4 of 1 degree of proof. If the sample contains more than 600 milligrams of solids, it must be distilled.

The actual proof must not be more than the stated proof or no less than 0.3 below the stated proof for solids less than 600 mg 100 mL, and no less than 0.5 below the stated proof for solids greater than 600 mg 100 mL. The actual alcohol content must be given to the nearest 0.5° o.

The analysis of individual chemical constituents in distilled spirits currently is performed using gas chromatography (gc) and high pressure liquid chromatography (hplc). Although other types of instrumental analyses have yielded much information regarding the chemical constituency of distilled spirits, the combination of gc and hplc has allowed hundreds of different chemical components of distilled spirits to be individually identified and accurately quantified.

The most common chromatogram in the distilled spirits industry is the fusel oil content. This consists of *n*-propyl alcohol, isobutyl alcohol, and isoamyl alcohol. Other common peaks are ethyl acetate, acetaldehyde, and methanol. The gc columns may be steel, copper, or glass packed column or capillary columns. Additional analyses include determinations of esters, total acids, fixed acids, volatile acids, solids or extracts (used to determine

obscuration), tannins, and furfural.

The high degree of sensitivity, selectivity, and efficiency of gas chromatography allows the elucidation of a complete profile of the volatile components of distilled spirits. The wide selection of chromatographic columns and techniques, such as gc-ms, gc-ftir, and gc-ms-ftir, has allowed the chemist to routinely identify and quantify individual constituents on a parts-per-billion level. The two most critical variables in the analysis of volatile components of distilled spirits by gas chromatography are the selection of a suitable chromatographic column and of the most appropriate detector.

Gas chromatographic analysis of distilled spirits has historically been performed using glass or metal columns supporting a Carbowax packing. This type of analytical system is still commonly used for quality control and routine measurements. Currently, gc analysis of distilled spirits has moved toward capillary gas chromatographic techniques. A narrow bore-fused silica tube lined with a specific coating serves to effect extremely efficient separation of the constituents of distilled spirits. The most commonly used chromatographic columns in these analyses are the DB-1, the DB-5, and the Carbowax columns.

The most favored gas chromatographic detectors for the analysis of distilled spirits are the flame ionization detector (FID) and the mass spectrometer detector. The flame ionization detector employs a hydrogen flame for the combustion of organic substances to produce electrons and ions that are collected on an anode. The resulting electrical current is proportional to the amount of the material burned. Mass spectrometric detection employs an electron beam to cause fragmentation of the chromatographic effluent. The fragments are collected and compared to the individually specific fragmentation patterns of known compounds.

Hplc techniques are used to routinely separate and quantify less volatile compounds. The hplc columns used to affect this separation are selected based on the constituents of interest. They are typically reverse phase or anion exchange in nature. The constituents routinely assayed in this type of analysis are those high in molecular weight or low in volatility. Specific compounds of interest include wood sugars, vanillin, and tannin complexes. The most common types of hplc detectors employed in the analysis of distilled spirits are the refractive index detector and the ultraviolet detector. Additionally, the recent introduction of the photodiode array detector is making a significant impact in the analysis of distilled spirits.

Advances in the technology of chemical analysis and the ability to analyze for trace amounts of complex compounds now make it possible to combine analytical information with sensory analysis to identify taste characteristics and facilitate process control.

Health and Safety Factors

Ethyl Carbamate. In November 1985, the Canadian Government indicated that it had detected ethyl carbamate *[51-79-6]* (urethane), a suspected carcinogen, in some wines and distilled spirits. Since that time, the U.S. distilled spirits industry has mounted a serious effort to monitor and reduce the amount of ethyl carbamate (EC) in its products. In December 1985, the Canadian Government set limits of 150 ppb in distilled spirits and 400 ppb in fruit brandies, cordials, and liqueurs. The FDA accepted a plan in 1987 from the Distilled Spirits Council of the United States (DISCUS) to reduce ethyl carbamate in whiskey to 125 ppb or less, beginning with all new production in January 1989.

Ethyl carbamate, $C_3H_7NO_2$, is developed naturally during the fermentation of alcoholic beverages. It also appears in foods such as bread and yogurt. Since ethyl carbamate is not easily distilled, its formation most likely involves a distillable precursor. The mechanism of ethyl carbamate formation probably involves cyanate produced from the oxidation of cyanide or from urea-based compounds in the beer. Cyanate reacts with alcohol to form ethyl carbamate as follows:

$$CH_3CH_2OH + HOCN \longrightarrow CH_3CH_2O-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$$

There are at least three gc methods employed by the ATF, industry, and the government to detect ethyl carbamate.

Distillers employ a somewhat unique process to make various products and have tailored approaches to control and reduce ethyl carbamate to their own particular process. Some of the methods used are the use of copper packing in the rectifying section of stills, increased frequency of cleaning stills and other equipment, and using a cool-down period in the cleaning procedure. Increased rectification also reduces ethyl carbamate. Keeping the system clean is critical to minimizing ethyl carbamate.

Based on an agreement with the FDA, all distilleries report their ethyl carbamate values by plant on a quarterly basis through DISCUS. Most distilleries always have been under the 125 ppb limit. Others, by controlling their process and by making some of the modifications mentioned above, have been able to reduce the concentration well below the limit (20–50 ppb). Although more remains to be done in the area of ethyl carbamate formation mechanisms, much progress has been made in monitoring, controlling, and significantly reducing ethyl carbamate in distilled spirits.

Packaging

Packaging for distilled spirits intended for domestic distribution is regulated by the Federal Bureau of Alcohol, Tobacco, and Firearms (ATF). This strict supervision establishes acceptable container size, labeling, and sealing requirements, as well as the disclosure of information on the shipping container. Furthermore, local and state distilled spirits' labeling and packaging requirements must also be met.

Several changes have occurred in these areas over the past few years. The addition of a health warning statement for each alcoholic beverage container and the change from proof to percent alcohol by volume has necessitated numerous label changes. Many distillers have also modified, redesigned, or changed their package to eliminate the Federal strip stamp that has long been commonplace for all distilled spirits. Most distillers have opted for a tamper evident closure, which has required changes to bottle molds and glassware, whereas some distillers are utilizing a tamper evident shrinkband to replace the strip stamp. These changes have been implemented primarily to comply with the regulations, lower the cost, and simplify the packaging of beverage alcohol.

The standard legal sizes, as outlined by the ATF for domestic distribution, are 1.75 L (59.2 fluid ounces), 1 L (33.8 fluid ounces), 750 mL (25.4 fluid ounces), 375 mL (12.8 fluid ounces), 200 mL (6.8 fluid ounces), 100 mL (3.4 fluid ounces, which is approved by a limited number of states), and 50 mL (1.7 fluid ounces). Individual states continue to limit the number and size of containers that are distributed within their jurisdiction. In some cases these do not coincide with all sizes available and authorized by the ATF.

In the past few years many changes have occurred in the packaging materials utilized for distilled spirits. Traditionally, distilled spirits have been packed primarily in glass containers of approved ATF sizes. Over the last 5–10 years, plastic containers, primarily poly(ethylene terephthalate) (PET), have been utilized by increasing numbers of distillers. Because of environmental concerns, the last two years have seen a change back to glass on some of these package sizes. However, the 50 mL miniature bottle continues to be primarily packed in PET plastic containers.

Most recently, greater concern has been placed on the increased use of bar codes. The basis for all bar code systems is the Uniform Product Code or UPC. Strict guidelines were developed by the Uniform Code Council and are enforced by the retail outlets. The purpose for the bar codes is for electronic data scanning and computerized pricing at the retail outlets. Recently, more and more emphasis is being placed on the use of bar codes throughout the distribution network. Shipping Container Symbology or SCS bar codes are now being requested on each case of distilled spirits.

A spinoff from the UPC bar code is the European Article Numbering (EAN) bar code system. EAN numbers are based on the UPC bar code guidelines. For distribution outside North America, these bar codes are unique and different in the number of characters per code and the computer data base related to each code.

In addition to the EAN bar code that appears on the consumer salable package, an EAN dispatch bar code has been established, similar to the SCS bar code, for shipping containers. The dispatch bar code on the shipping containers enable distributors to scan individual cases throughout the distribution network to assure that the proper products are being selected and shipped, as well as serving as an inventory control. Eventually, the use of these bar code systems will enable electronic data interchange for ordering and releasing. These systems are already in place in food grocery systems as well as consumer durable goods distribution networks. The distilled spirits industry is challenged with developing economical ways of complying with these new bar code system requirements.

Deposit refund labeling is another requirement recently introduced to the distilled spirits industry. Currently, legislation in Iowa, Vermont, and Maine requires distillers to comply with labeling requirements to disclose the deposit refund value for each state on their label. Other states are considering similar forms of deposit refund legislation for distilled spirits. This will offer another challenge for the packaging of distilled spirits. The environmental concerns extend further than deposit refunds and offer the greatest packaging challenge in the near future. Packaging components that are produced and supplied to distillers should adhere to Environmental Protection Agency (EPA) guidelines. These guidelines limit the intentional use of heavy metals for the production of packaging materials. The use of inks, coatings, and other materials for packaging of distilled spirits must not contain more than 5 ppm of defined heavy metals such as lead, mercury, selenium, chromium, silver, and cadmium. Additionally, no trace amounts of these elements should be found in the product itself. This requirement has nearly eliminated the use of crystal decanters or ceramics that were commonly used for decorative package sales in the past.

The packaging of distilled spirits has become more complex with both the demands for higher efficiencies of the production facilities within the industry, and the request by marketing and sales departments for higher flexibility to provide customers with greater value on products.

The distilled spirits industry has an ongoing development of new products and line extensions using more diverse and less traditional types of packaging materials. In addition, there is a significant thrust on reducing the weight of all glass and plastic packaging to lower the cost of goods and shipping.

Flavor Applications

Flavoring beverage alcohol products presents some interesting challenges since ethyl alcohol itself has flavor. In high proof beverages (ie, over 80°), which contain pure alcohol, and not whiskey or rum that have inherent flavor characteristics, flavors must be added to help smooth out the harshness and singularity of the flavor profile. At proofs below 10°, the ethyl alcohol flavor is often below optimum sensory profiles. Flavors can be used to supplement a desired aroma profile. The same flavor has different sensory characteristics at various proof levels. Higher concentrations of flavor are generally required in higher proof products to compete with the ethyl alcohol flavor. The sources and types of distilled spirits (brandy, whiskey, rum, and spirits) have various analytical profiles that combine differently with specific flavors. It is not unusual to find certain characteristics of a flavor out of balance when applied to a base that contains the same chemicals. When organic-based flavors are applied to an ethyl alcohol base, there is the potential for several chemical reactions. Ethyl alcohol reacts with aldehydes to form the corresponding acetal. This reaction occurs more readily at higher proofs and in acid conditions such as those found in most cordials. This is in many cases a desirable reaction and was described years ago as "marrying."

Since the acetal exists in equilibrium with the aldehyde, it is possible for the aldehyde to be released when water is added in a mixed drink, changing the balance and giving a burst of freshness to a mixed drink. Ethyl esters of terpene alcohols in citrus oils and other botanicals, plus the ethyl esters of fatty and volatile acids, are formed during prolonged exposure to ethyl alcohol. Certain beverage alcohol products that need to contain milk, eggs, or other protein containing materials must be developed carefully and the added flavors must be considered to prevent the precipitation of the protein and separation of the product.

Most flavors that are designed for beverage alcohol products use ethanol as the primary solvent for the flavor. Glycerol *[56-81-5]*, propylene glycol *[57-55-6]*, and water are other common solvents in liquid flavors. Some beverage alcohol concepts require the addition of an emulsified flavor, either as a vehicle to solubilize the oils in the beverage or as a deliberate attempt to cloud the product. This can best be accomplished at lower proofs with the alcohol breaking the emulsion.

Many beverage alcohol products depend heavily on the addition of compounded flavors, distillates, percolates, and extracts to carry the organoleptic profile of the product. Cordials, liqueurs, and schnapps at various proofs, such as Creme de Cocoa, Peppermint Schnapps, fruit-flavored cordials and schnapps, and spirit coolers are examples. Flavored whiskeys, rums, and brandies often contain blenders and merger flavors which assist in diminishing the flavor variances encountered because of crop and storage conditions. Generally, flavor applications in food and beverages are specific to the type of end product that the flavor is used to enhance. For instance, when flavoring a bakery item, flavors must be able to compensate for high oven temperatures and other inherent flavors present in the food. More strikingly, foods that are extruded must use flavors that can withstand the extreme temperatures used during processing. Likewise, beverage alcohol flavor applications require the consideration of many factors that affect the finished product. These include proof, inherent flavors, added flavors, source of ethanol, and overall composition.

Future Developments

The decline in distilled spirits consumption is likely to continue, but will be somewhat ameliorated by the increased consumer interest in high price premium products and the increased activity in the international markets. For example, Japan is importing significant amounts of American bourbon, a trend that will probably continue.

The trend toward lower proof beverages will also likely continue because of new consumer preferences, cost reduction, and tax savings opportunities. Pressures to improve production efficiencies and lower costs will increase and new technology must play a greater role in this area. Distilled beverages have been produced for several thousands of years and will continue to be consumed in an ever increasing variety of forms and packages.

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BIACETYL.

See Ketones.

BILE CONSTITUENTS.

See Meat products.

BINARY CYCLES.

See Power generation.

BIOASSAY.

See Automated instrumentation; Immunoassay; Medical diagnostic reagents.

BIOCIDES.

See Industrial antimicrobial agents.

BIOCOMPATIBLE MATERIALS.

See Prosthetic and biomedical devices; Sutures.

BIODEGRADABLE POLYMERS.

See Plastics, environmentally degradable.

BIOGENIC AMINES.

See Neuroregulators; Opiods, endogenous.

BIOMASS CHEMICALS.

See Chemurgy; Fuels from biomass.

BIOMEDICAL AUTOMATED INSTRUMENTATION.

See Automated instrumentation.

BIOPOLYMERS

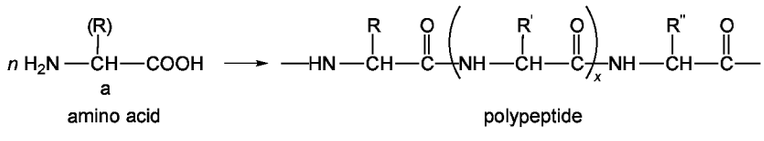
Survey,
Analytical techniques,

SURVEY

Biopolymers are the naturally occurring macromolecular materials that are the components of all living systems. There are three principal categories of biopolymers, each of which is the topic of a separate article in the *Encyclopedia:* proteins (qv); nucleic acids (qv); and polysaccharides (see CARBOHYDRATES; MICROBIAL POLYSACCHARIDES). Biopolymers are formed through condensation of monomeric units; ie, the corresponding monomers are amino acids (qv), nucleotides, and monosaccharides, for proteins, nucleic acids, and polysaccharides, respectively. The term biopolymers is also used to describe synthetic polymers prepared from the same or similar monomer units as are the natural molecules.

In addition to being necessary for all forms of life, biopolymers, especially enzymes (proteins), have found commercial applications in various analytical techniques (see AUTOMATED INSTRUMENTATION, CLINICAL CHEMISTRY; AUTOMATED INSTRUMENTATION, HEMATOLOGY; BIOPOLYMERS, ANALYTICAL TECHNIQUES; BIOSENSORS; IMMUNOASSAY); in synthetic processes (see ENZYME APPLICATIONS, INDUSTRIAL; ENZYME APPLICATIONS IN ORGANIC SYNTHESIS); and in prescribed therapies (see ENZYME APPLICATIONS, THERAPEUTICS; IMMUNOTHERAPEUTIC AGENTS; VITAMINS). Other naturally occurring biopolymers having significant commercial importance are the cellulose (qv) derivatives, eg, cotton (qv) and wood (qv), which are complex polysaccharides.

Proteins. The most abundant and physiologically diverse natural biopolymers are proteins, which make up enzymes, hormones, and structural material such as hair, skin, and connective tissue. The monomer units of natural proteins, α-amino acids, condense to form dipeptides, tripeptides, polypeptides, and proteins.

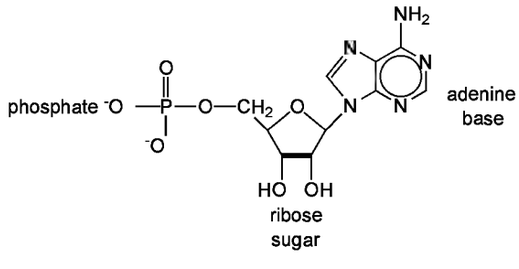


There are approximately 20 common naturally occurring amino acids, hence 20 different R groups that appear as pendents on the polyamide chain. Many other amino acids have been isolated or prepared, each representing a variation in R. The number of isomeric structures is myriad. Protein biosynthesis is mediated by other biopolymers, the nucleic acids.

The amide linkage between monomer units in a protein is called a peptide bond. Peptides and polypeptides, which often exhibit biological activity (see ANTIBIOTICS, PEPTIDES; NEUROREGULATORS), are smaller than proteins. Although the differentiation between polypeptide and protein is somewhat arbitrary, the usual distinction is drawn around 100 monomer units. Proteins are also characterized by higher levels of structure resulting from internal interactions.

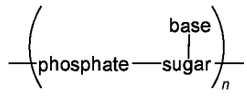
Proteins may consist exclusively of a polymeric chain of amino acids; these are the simple proteins. Quite often some other chemical component is covalently bonded to the amino acid chain. Glycoproteins and lipoproteins contain sugar and lipid components, respectively. Porphyrins are frequently associated with proteins, eg, in hemoglobin. Proteins bound to other chemical components are called conjugated proteins. Most enzymes are conjugated proteins.

Nucleic Acids. Nucleic acids are polynucleotides; that is, they are condensation polymers of nucleotide monomers. A nucleotide is a three-component system, ie, a combination of a sugar, a phosphate, and a nitrogenous base residue. Adenosine monophosphate is an example:



A two-component sugar-base unit is called a nucleoside, eg, adenosine. Nucleosides and their derivatives are important pharmaceutically (see ANTIBIOTICS, NUCLEOSIDES AND NUCLEOTIDES; ANTIVIRAL AGENTS).

Polymerization of nucleotides occurs through the sugar and phosphate groups so that the polymers consist of a sugar-phosphate backbone having pendent bases.



The sugars are typically ribose (ribonucleic acids, RNA), or 2-deoxyribose (deoxyribonucleic acids, DNA). There are five common bases in nucleic acids: adenine (A); thymine (T); uracil (U); cytosine (C); and guanine (G). DNA polymers incorporate the four bases, A, T, C, and G, and RNA, the set A, U, C, and G.

Nucleic acids are the molecules of the genetic apparatus. They direct protein biosynthesis in the body and are the raw materials of genetic technology (see GENETIC ENGINEERING). Most often polynucleotides are synthesized microbiologically, or at least enzymatically, but chemical synthesis is possible.

Polysaccharides. Polysaccharides, also called glycans, are the nutrient and structural materials of plants. They are a principle part of the carbohydrate portion of the biomass. The most prevalent monomeric carbohydrate is glucose. Common polysaccharides are all polymers of glucose (Fig. 1). The distinctions between these homopolymers arise from the different ways in which the monomer units are hooked together in polyacetal chains. Starch (qv), plant nutrient material, is composed of two polysaccharides: α-amylose and amylopectin. α-Amylose is linear because of exclusive α (1 → 4) linkages, whereas amylopectin is branched because of the presence of α (1 → 6) as well as α (1 → 4) links. The terms linear and branched refer only to primary structure.

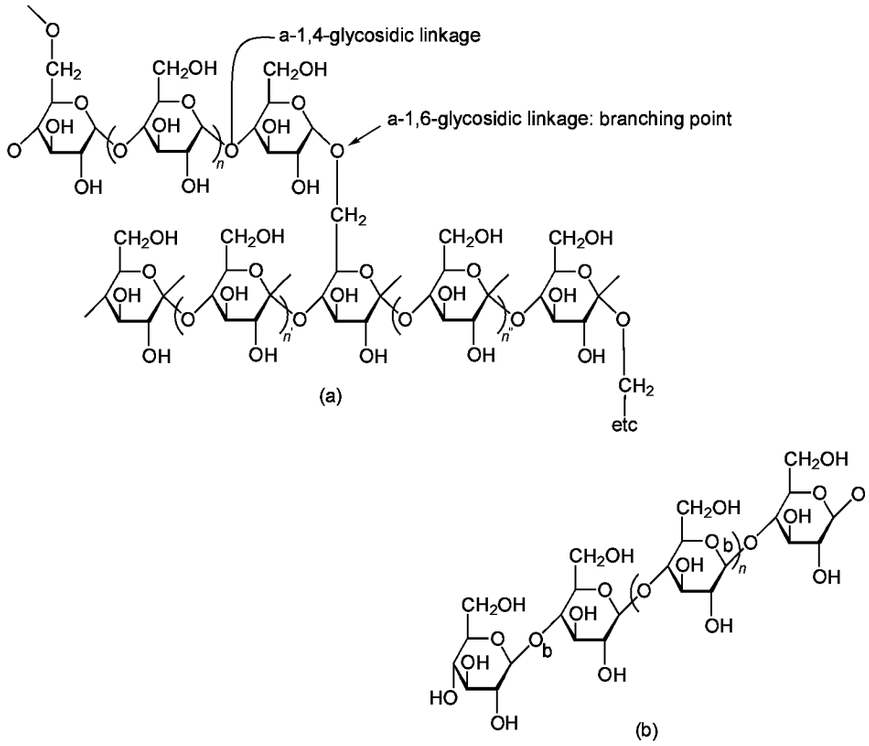


Fig. 1. Primary structures of some common polysaccharides. (**a**) Alpha-glycoside linkages characterize amylose, amylopectin, and glycogen; (**b**) cellulose has β-glycoside linkages.

Plant structural material is the polysaccharide cellulose, which is a linear β (1 → 4) linked polymer. Some structural polysaccharides incorporate nitrogen into their molecular structure; an example is chitin, the material which comprises the hard exoskeletons of insects and crustaceans. Chitin is a cellulose derivative wherein the OH at C-2 is replaced by an acetylated amino group ($-NHCOCH_3$). Microbial polysaccharides, of which the capsular or extracellular (exopolysaccharides) are probably the most important class, show more diversity both in monomer units and the nature of their linkages.

As in the case of proteins, which may be simple or conjugated, oligosaccharides or polysaccharide chains may be covalently bonded to noncarbohydrate chemical components (see ANTIBIOTICS, OLIGOSACCHARIDES). For example, carbohydrate–protein combinations are called glycoproteins or proteoglycans depending on which chemical moiety predominates; the latter are also called mucopolysaccharides. Peptidoglycans and lipopolysaccharides are other complex polysaccharides. Murein, which is found in bacterial cell walls, consists of parallel polysaccharide chains cross-linked by short peptide chains. Wood (qv) is cellulose, a polysaccharide, linked to lignin (qv).

Obviously, much more detail concerning these materials will be found in the *Encyclopedia* articles cited.

ANALYTICAL TECHNIQUES

Analytical techniques that utilize biopolymers, ie, natural macromolecules such as proteins, nucleic acids, and polysaccharides that compose living substances, represent a rapidly expanding field. The number of applications is large and thus uses herein are limited to chiral chromatography, immunology, and biosensors.

Biopolymers in Chiral Chromatography

Biopolymers have had a tremendous impact on the separation of nonsuperimposable, mirror-image isomers known as enantiomers. Enantiomers have identical physical and chemical properties in an achiral environment except that they rotate the plane of polarized light in opposite directions. Thus separation of enantiomers by chromatographic techniques presents special problems, whereas diastereomers have different chemical and physical properties and may be separated by more conventional methods (see CHROMATOGRAPHY). Direct chiral resolution by liquid chromatography (lc) involves diastereomeric interactions between the chiral solute and the chiral stationary phase. Because biopolymers are chiral molecules and can form diastereomeric interactions with chiral solutes, they are ideal for use as chiral stationary phases. This property has led to a rapid growth of chromatographic stationary phases utilizing biopolymers to separate chiral molecules.

Cyclodextrin Chromatographic Phases.

Properties and Structure. Cyclodextrins (CDs) are natural macrocyclic polymers of glucose that contain from 6 to 12 D-(+)-glucopyranose units bonded through α-(1,4)-linkages. They are chiral, torodial-shaped molecules with all the glucose units in a C-1 (D) chair conformation (1,2). The structure of β-cyclodextrin is shown in Figure 1. The mouth of the molecule, facing outward, has the larger circumference of the openings, and contains the secondary hydroxyl groups on C-2 and C-3 of the glucose molecule. The primary hydroxyl groups, those attached to C-6 of the glucose unit, are on the opposite end of the cyclodextrin, which forms the smaller opening. The cyclodextrin molecule is therefore shaped like a truncated cone. The primary hydroxyl groups on the truncated end can rotate to block the cavity partially, whereas the secondary hydroxyl groups at the mouth are held relatively rigid. The interior of the cavity consists of two rings of C–H groups with a ring of glucosidic oxygens in between. This makes the interior relatively hydrophobic in comparison to polar solvents such as water. The mouth of the cyclodextrin cavity, however, is hydrophilic. A Greek letter is used to denote the number of glucose units in the cyclodextrin molecule. For example, α for six, β for seven, γ for eight, and so on.

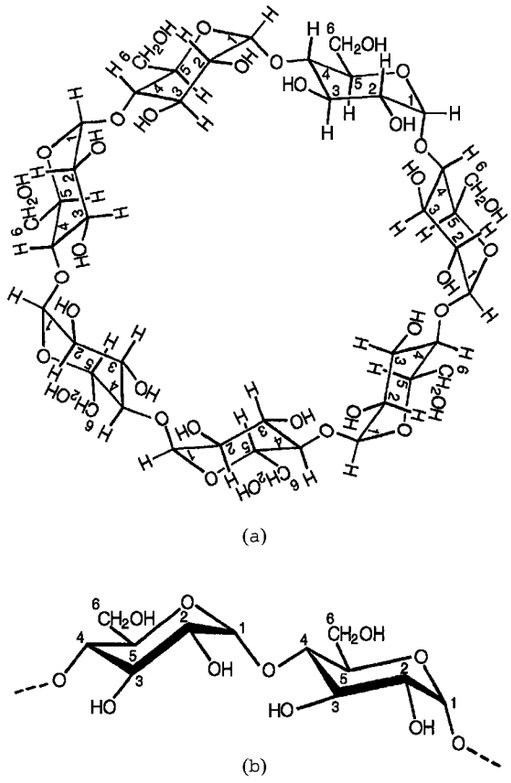


Fig. 1. Structural diagram of (**a**) β-cyclodextrin and (**b**) two of the glucopyranose units illustrating details of the α-(1,4) glycosidic linkage, C-1 (D) chair conformation, and the numbering system employed to describe the ring system.

Some physical properties of the four most common cyclodextrins are listed in Table 1 (3). Other important properties are (*1*) cyclodextrins are nonreducing; (*2*) glucose is the only product of acid hydrolysis; (*3*) molecular weights are always integral numbers of 162.1, the value for glucose; (*4*) cyclodextrins are nontoxic; and (*5*) they do not appreciably absorb ultraviolet (uv) or visible light.

Table 1. Physical Properties of Cyclodextrins

Cyclodextrin	CAS Registry Number	Molecular formula	Number of glucose units	Cavity diameter, nm[a] External	Cavity diameter, nm[a] Internal	Aqueous solubility, *M*
α-CD	*[10016-20-3]*	$C_{3}H_{0}O_{30}$	6	1.37	0.57	0.114

β-CD	[7585-39-9]	$C_{42}H_{70}O_{35}$	7	1.53	0.78	0.016
γ-CD	[17465-86-0]	$C_{48}H_{80}O_{40}$	8	1.69	0.95	0.179
δ-CD	[85220-53-7]	$C_{54}H_{90}O_{45}$	9			v sol

[a] Depth of cavity is 0.78 nm for each cyclodextrin.

The enzyme responsible for producing cyclodextrins from starch, cyclodextrin transglycosylase (CTG), does not cleave a specific number of glucose units from starch. Homologues from 6 to 12 glucose units may be obtained as mixtures having small amounts of branched cyclic molecules and branched open-chain dextrins. A five-membered or smaller dextrin ring has never been obtained. This is most likely attributable to the considerable strain present in small rings.

Several procedures are used to control the ratios of cyclodextrins produced. One is addition of a substance to the reaction mixture that can greatly affect the formation of one specific cyclodextrin over another. For example, in the presence of 1-decanol and 1-nonanol, α-cyclodextrin is produced almost exclusively whereas hexane or toluene promote the production of β-cyclodextrin. Conversely both cyclodextrins are produced simultaneously in the presence of 1-heptanol (2,4).

Immobilization. The ability of cyclodextrins to form inclusion complexes selectively with a wide variety of guest molecules or ions is well known (1,2) (see INCLUSION COMPOUNDS). Cyclodextrins immobilized on appropriate supports are used in high performance liquid chromatography (hplc) to separate optical isomers. Immobilization of cyclodextrin on a solid support offers several advantages over use as a mobile-phase modifier. For example, as a mobile-phase additive, β-cyclodextrin has a relatively low solubility. The cost of γ- or α-cyclodextrin is high. Furthermore, when employed in thin-layer chromatography (tlc) and hplc, cyclodextrin mobile phases usually produce relatively poor efficiencies.

Cyclodextrin stationary phases utilize cyclodextrins bound to a solid support in such a way that the cyclodextrin is free to interact with solutes in solution. These bonded phases consist of cyclodextrin molecules linked to silica gel by specific nonhydrolytic silane linkages (5,6). This stable cyclodextrin bonded phase is sold commercially under the trade name Cyclobond (Advanced Separation Technologies, Whippany, New Jersey). The vast majority of all reported hplc separations on CD-bonded phases utilize this media which was also the first chiral stationary phase (csp) developed for use in the reversed-phase mode.

Applications. The first widely applicable lc separation of enantiomeric metallocene compounds was demonstrated on β-CD bonded-phase columns. Thirteen enantiomeric derivatives of ferrocene, ruthenocene, and osmocene were resolved (7). Retention data for several of these compounds are listed in Table 2, and Figure 2**a** shows the lc separation of three metallocene enantiomeric pairs. β-Cyclodextrin bonded phases were used to resolve several racemic and diastereomeric 2,2-binaphthyldiyl crown ethers (9). These compounds do not contain a chiral carbon but still exist as enantiomers because of the staggered position of adjacent naphthyl rings, and a high degree of chiral recognition was attained for most of these compounds (9).

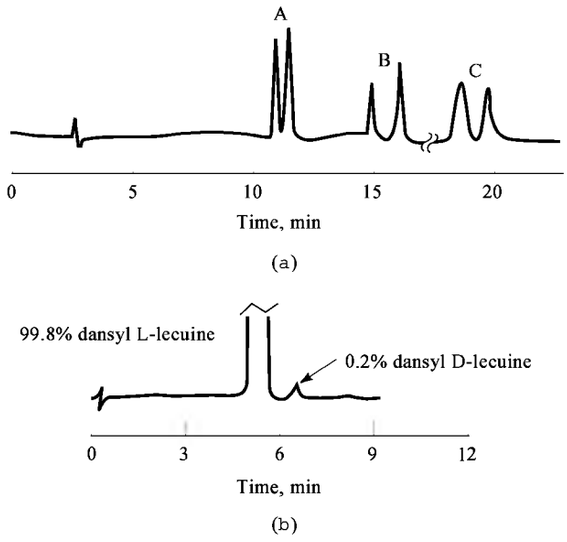


Fig. 2. Chromatogram showing (**a**) the lc separation of A, (±) (*S*)-(1-ferrocenyl-ethyl)thioethanol; B, (±) 1-ferrocenyl-1-methoxyethane; and C, (±) 1-ruthenocenylethanol, on a 25-cm β-cyclodextrin column (see Table 2), and (**b**) the potential use of a β-cyclodextrin column to determine optical purity when one of the enantiomers is present at very low concentration (5,7).

Courtesy of Preston Publications.

Table 2. Retention Data for Racemic Compounds Separated on a β-Cyclodextrin Stationary Phase[a]

Compound	CAS Registry Number	Molecular formula	k'[b]	α[c]	R_f[d]
		Complexes			
1-ferrocenyl-1-methoxy-ethane		$C_{13}H_{17}FeO$	3.8	1.12	1.58
(*S*)-(1-ferrocenylethyl)-thioethanol		$C_{14}H_{17}FeSO$	3.0	1.23	2.13
1-ruthenocenylethanol		$C_{12}H_{14}RuO$	4.6	1.11	1.56
alanine β-naphthylamide	[74144-49-3]	$C_{13}H_{14}N_2O \cdot HCl$	5.1	1.20	2.0
dansyl-leucine	[102783-70-0]	$C_{18}H_{24}N_2O_4S \cdot C_{13}H_{13}N$	3.0	1.40	2.4
dansylphenylalanine	[42808-06-0]	$C_{21}H_{22}N_2O_4S \cdot C_{13}H_{13}N$	3.1	1.23	1.1
		β-Adrenergic blocker			
propranolol hydro-chloride	[3506-09-0]	$C_{16}H_{21}NO_2 \cdot HCl$	2.78	1.04	1.40
		Antihistamine			
chlorpheniramine	[132-22-19]	$C_{16}H_{19}ClN_2$	5.86	1.07	1.51
		Sedative–anticonvulsants			
mephenytoin	[50-12-4]	$C_{12}H_{14}N_2O_3$	0.48	1.33	1.83
mephobarbital	[115-38-8]	$C_{13}H_{14}N_2O_3$	14.80	1.14	1.60

		Nonsteroidal antiinflammatory			
ketoprofen	*[22071-15-4]*	$C_{16}H_{14}O_3$	7.67	1.06	1.24

[a] Refs. 4, 5, and 8.

[b] k′ is the capacity factor for the first eluting isomer.

[c] α is the selectivity factor and is the ratio of the capacity factor of the last eluting isomer to the first eluting isomer.

[d] R_s is the resolution factor. $R_s = 2$ (distance between peaks) (sum of the bandwidths of the two peaks).

The β-CD column exhibits excellent selectivity for enantiomers of certain amino acid derivatives. Underivatized amino acids are apparently too small to bind tightly to the β-CD cavity and show no enantiomeric resolution. When a substituent such as a dansyl group is present on the amino acid, strong inclusion complexes with β-CD are formed and baseline separation is achieved (see Table 2) (10). Either the amino or the carboxylate group of the amino acid can be derivatized to obtain chiral recognition. Derivatization of both groups, however, tends to reduce chiral recognition. It is possible to detect as little as 0.2% of one enantiomer in a racemic mixture as shown in Figure **2b,** thus providing an extremely sensitive test of optical purity (5).

Table 2 gives chromatographic data for different classes of enantiomeric drugs resolved by β-CD bonded phases (8). Drugs for which resolution factors (R_s) greater than 1.0 were obtained include mephenytoin, ketoprofen, chlorpheniramine, and the barbiturates mephobarbital and hexobarbital. Cyclodextrin-bonded phases provide a rapid and specific technique for the pharmacological evaluation of racemic drugs.

Many diastereomers, geometric isomers, and epimers can be successfully resolved using cyclodextrin phases (5,10). For example, the four epimers of estriol *[50-27-1]*, $C_{18}H_{24}O_3$, were separated using β-CD, and *cis*-benzo(*a*)pyrene and *trans*-benzo(*a*)pyrene were completely resolved on a γ-CD column. Diastereomeric drugs such as the cinchona alkaloids (qv) and antiestrogens have also been separated. Cyclodextrin columns are also of great utility in separating structural isomers such as the ortho-, meta-, and para- isomers of nitroaniline, xylene, cresols, nitrophenols, and substituted benzoic acids (11). Cyclodextrin bonded phases are used as nonconventional reversed phases for routine analyses as a result of the unusual selectivity of the cyclodextrin columns. Uses in routine analyses include the separation of a series of barbiturates, mycotoxins, polycyclic aromatic hydrocarbons, vitamins (qv) and selected dipeptides (12). Cyclodextrin stationary phases can be used in the normal-phase mode with hexane–isopropanol mobile phases. Solutes adsorb to the hydroxyl groups on the outside of the cyclodextrin, rather than forming inclusion complexes. Separations in the normal-phase mode tend to be analogous to those of diol columns.

Mechanism of Separation. There are several requirements for chiral recognition. (*1*) Formation of an inclusion complex between the solute and the cyclodextrin cavity is needed (4,10). This has been demonstrated by performing a normal-phase separation, eg, using hexane–isopropanol mobile phase, on a β-CD column. The enantiomeric solute is then restricted to the outside surface of the cyclodextrin cavity because the hydrophobic solvent occupies the interior of the cyclodextrin. (*2*) The inclusion complex formed should provide a relatively "tight fit" between the hydrophobic species and the cyclodextrin cavity. This is evident by the fact that β-CD exhibits better enantioselectivity for molecules the size of biphenyl or naphthalene than it does for smaller molecules. Smaller compounds are not as rigidly held and appear to be able to move in such a manner that they experience the same average environment. (*3*) The chiral center, or a substituent attached to the chiral center, must be near to and interact with the mouth of the cyclodextrin cavity. When these three requirements are fulfilled the possibility of chiral recognition is favorable.

The unidirectional 2- and 3-hydroxyl groups located at the mouth of the cyclodextrin cavity appear to be of particular importance in chiral recognition. This is seen in Figure 3, which shows computer-generated projections of the lowest free-energy inclusion complexes of (*R*)- and (*S*)-propranolol with β-CD (8). The (*R*)- and (*S*)-propranolol are placed identically inside the cyclodextrin cavity and the hydroxyl groups attached to the chiral carbon for the enantiomers are placed in the same position for ideal hydrogen bonding to the 3-hydroxyl group of the cyclodextrin. Important differences exist between the complexes with respect to the secondary amine group. In the (*R*) complex the respective bond distances between the nitrogen and the cyclodextrin 2- and 3-hydroxyl groups are 0.33 and 0.28 nm, respectively. This allows for two reasonable hydrogen bond interactions. The same amine group in the (*S*)-propranolol complex is positioned less favorably for hydrogen bonding: closest bond distances are 0.38 and 0.45 nm, respectively. These models suggest that (*R*)-propranolol can preferentially interact with β-cyclodextrin in a way that the (*S*)-isomer cannot, resulting in chiral recognition by the cyclodextrin molecule. These findings agree with the three-point attachment concept introduced in the 1950s (13).

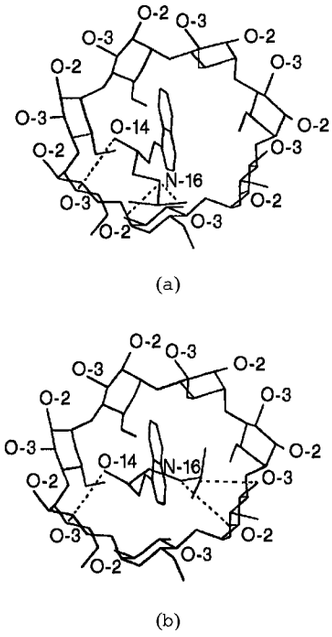


Fig. 3. Computer projections of β-cyclodextrin inclusion complexes of (**a**) (*R*)-propranolol and (**b**) (*S*)-propranolol from x-ray crystallographic data. Dotted lines represent potential hydrogen bonds (see text). The configurations shown represent the optimal orientation of each isomer on the basis of the highest degree of hydrogen bonding and complexation (8).

α_1-Acid Glycoprotein Chromatographic Phases.

Properties and Structure. α_1-Acid glycoprotein (α_1-AGP) has a molecular mass of about 41,000 and consists of a peptide chain having 181 amino acid residues and five carbohydrate units (14,15). Two cystine disulfide cross-linkages connect residues 5 and 147 and residues 72 and 164. The carbohydrate units comprise 45% of the molecule and contain sialic acid, hexosamine, and neutral hexoses. In phosphate buffer the isoelectric point of the

protein is 2.7. AGP is a very stable protein and tolerates organic solvents as well as high temperatures. AGP columns may be used over a wide pH range without being denatured. Denaturation, as measured by changes in the optical rotation of the molecule, may be caused by boiling in distilled water or adding 10 *M* LiBr, 10 *M* urea, or 5 *M* HCl (14).

Immobilization. The solid-phase support used for bonding AGP is silica gel. The general preparation is based on bonding the protein by charge forces to diethylaminoethylsilica followed by a cross-linking procedure (16). A final reduction to secondary amines is performed using cyanoborohydride. The silica has a particle diameter of 10 μm, a large pore volume, and a large surface area. The commercially available EnantioPac AGP column (LKB Products, Bromma, Sweden) is manufactured using this procedure. A second generation AGP column, Chiral-AGP (ChromTech AB, Norsburg, Sweden), uses covalent linkage of the protein onto silica with cross-linking of adjacent protein molecules (17,18). This latter packing contains 5 μm spherical silica particles having a smaller pore volume and a smaller surface area giving a stationary phase that is more mechanically stable and resistant to hydrolytic attack. Bonding capacity of the chiral phase and loading capacity of solute are directly dependent on the amount of protein that is bound. The amount of AGP bound on the silica depends on the bonding technique and on the accessible surface area of the silica.

Applications. Retention and selectivity of solutes on AGP is regulated by the concentration and properties of modifiers in the aqueous-based mobile phase. Retention and enantioselectivity usually decrease with increasing concentration of uncharged organic modifiers such as methanol, ethanol, 2-propanol, and acetonitrile in the mobile phase. However, in some cases, enantioselectivity can be improved by adding uncharged modifiers to the mobile phase (19). For example, addition of 2-propanol as an organic modifier gave improved chiral resolution for mephenytoin *[50-12-4]*, $C_{12}H_{14}N_2O_2$, and methylphenobarbital. On the other hand, the enantioselectivity for the tertiary amines mepivacaine and bupivacaine is unaffected by additions of up to 8% of propanol to the mobile phase, despite the fact that the retention of these solutes decreases markedly under these conditions (18) (see ANESTHETICS; HYPNOTICS, SEDATIVES, AND ANTICONVULSANTS).

Column retention is generally increased if the modifier has a charge opposite to that of the solute; a modifier having the same charge as the solute generally decreases retention. For some compounds the addition of charged modifiers is essential to achieve chiral recognition. The fenthiazin derivative, propiomazine *[362-29-8]*, $C_{20}H_{24}N_2OS$, was not resolved on an AGP column when phosphate buffer, pH 7.55, was used as the mobile phase. After addition of 1 m*M* of the tertiary amine *N,N*-dimethyloctylamine (DMOA) to the mobile phase, however, the enantiomers of propiomazine were baseline resolved (20) and longer retention times were obtained. Increase in retention is believed to be caused by competition between the solute and DMOA in binding to the AGP. The changes in selectivity are believed to result from reversible changes in the conformation of AGP brought about by changes in pH. Similar effects on selectivity and retention have also been observed by addition of tetrapropylammonium bromide or tetrabutylammonium bromide (15,16,21,22).

Changes in the pH and temperature of the mobile phase can have a significant effect on both retention and selectivity. Changing the pH of the mobile phase has a profound effect on retention and selectivity for basic, acidic, and nonprotolytic compounds. For example, the separation factors for hexobarbital *[56-29-1]*, $C_{12}H_{1}N_2O_3$ (weakly acidic) and metoprolol *[37350-58-6]*, $C_{15}H_{25}NO_3$ (basic) (see CARDIOVASCULAR AGENTS), increase with increasing pH, but the enantioselectivity for stronger acids such as 2-phenoxypropionic acid ($pK_a = 4.6$) generally decreases (21). Column temperature also strongly influences retention and enantioselectivity. It has been generally reported that retention, resolution, and separation factors decrease with increasing temperature, whereas efficiency increases.

AGP columns have wide application for the direct separation of enantiomers of many different classes of drugs, amines, acids, and nonprotolytic compounds (18,23). Acidic drugs resolved include ibuprofen *[15687-27-1]*, $C_{13}H_{18}O_2$, ketoprofen *[22071-15-4]*, $C_{1}H_{14}O_3$, and naproxen *[22204-53-1]*, $C_{14}H_{14}O_3$, and basic drugs such as disopyramide *[3737-09-5]*, $C_{21}H_{29}N_3O$, tropicamide *[1508-75-4]*, $C_{17}H_{20}N_2O_2$, atropine *[51-55-8]*, $C_{17}H_{23}NO_3$, and homatropine *[87-00-3]*, $C_{1}H_{21}NO_3$, have also been separated (21,24). Table 3 lists some racemic compounds that have been completely resolved using a Chiral-AGP column (18). The AGP columns are also commonly used in the determination of enantiomers present at low concentrations in biological fluids such as plasma and urine (19,25). Metoprolol was extracted from plasma and injected on a Chiral-AGP column for separation (25). It was possible to measure as little as 2 nmol L plasma using fluorescence detection after separation.

Table 3. Baseline-Resolved Racemic Compounds Using Chiral-AGP

Compound	CAS Registry Number	Molecular formula	k′[a]	α[b]
alprenolol	*[13655-52-2]*	$C_{15}H_{23}NO_2$	17.9	1.19
atenolol	*[2180-92-9]*	$C_{14}H_{22}N_2O_3$	2.91	1.36
bupivacaine	*[29122-68-7]*	$C_{18}H_{28}N_2O$	6.66	1.29
cyamemazine	*[3546-03-0]*	$C_{19}H_{21}N_3S$	5.95	1.55
ephedrine	*[90-81-3]*	$C_{10}H_{15}NO$	3.86	1.34
ketamine	*[6740-88-1]*	$C_{13}H_{1}ClNO$	7.00	1.26
metoprolol	*[37350-58-6]*	$C_{15}H_{25}NO_3$	4.72	1.26
oxprenolol	*[6452-71-7]*	$C_{15}H_{23}NO_3$	16.1	1.29
pheniramine	*[86-21-5]*	$C_{1}H_{20}N_2$	11.3	1.33
pindolol	*[13523-86-9]*	$C_{14}H_{20}N_2O_2$	13.9	1.21
verapamil	*[52-53-9]*	$C_{27}H_{38}N_2O_4$	15.6	1.32
warfarin	*[81-81-2]*	$C_{10}H_{1}O_4$	8.18	1.39

[a] k′ is the capacity factor for the first eluting isomer.
[b] α is the selectivity factor See Table 2.

Mechanism of Separation. Whereas the scientific basis of separation is well documented, ie, differences in binding between drug enantiomers and proteins, the mechanism for chiral recognition is not clearly understood. It is well known that the conformation of a native protein in solution can be altered by addition of organic modifiers and changes in pH. It is assumed that the AGP molecule has a high degree of flexibility even after bonding to the silica surface. Therefore adding modifiers to the mobile phase can alter the AGP molecule so that new chiral phases having different binding properties are induced (18,21).

Bovine Serum Albumin Chromatographic Phases.

Properties and Structure. Bovine serum albumin (BSA) is a globular protein having a molecular mass of 66,210. It consists of 581 amino acids in a single chain, and 17 intrachain disulfide bridges form nine double loops (26). Having an isoelectric point of 4.7, BSA is a relatively acidic protein. It is highly soluble in water, but like most globular proteins it precipitates from solution at high salt concentrations. BSA exhibits hydrophobic character and numerous examples of organic compounds binding to albumins have been reported (27). Whereas hydrophobic interactions contribute greatly to the total affinity of organic ligands for BSA, there are other contributions to consider, mainly electrostatic interactions, hydrogen bonding, and charge-transfer processes.

The first observation of the enantioselective properties of an albumin was made in 1958 (28) when it was discovered that the affinity for L-tryptophan exceeded that of the D-enantiomer by a factor of approximately 100. This led to more studies in 1973 of the separation of DL-tryptophan *[54-12-6]*, $C_{11}H_{12}N_2O_2$, on BSA immobilized to Sepharose (29). After extensive investigation of the chromatographic behavior of numerous racemic compounds under different mobile-phase conditions, a BSA-SILICA hplc column (Resolvosil-R-BSA, Macherey-Nagel GmvH, Duren, Germany) was

introduced in 1983.

Retention and stereoselectivity on the BSA columns can be changed by the use of additives to the aqueous mobile phase (30). Hydrophobic compounds generally are highly retained on the BSA, and a mobile-phase modifier such as 1-propanol can be added to obtain reasonable retention times. The retention and optical resolution of charged solutes such as carboxylic acids or amines can be controlled by pH and ionic strength of the mobile phase.

Applications. Various *N*-derivatives of amino acids (qv) are resolvable on BSA columns. These *N*-amino acid derivatives include benzenesulfonyl-, phthalimido-, 5-dimethylamino-1-naphthalenesulfonyl- (DANSYL-), 2,4-dinitrophenyl- (DNP-), and 2,3,6-trinitrophenyl- (TNP-) derivatives (30). Amines such as Prilocain, (±)-2-(propylamino)-*o*-propiono-toluidide, a local anesthetic (Astra Pharm. Co.), are also resolved on BSA. The aromatic amino acids DL-tryptophan, 5-hydroxy-DL-tryptophan, DL-kynurenine *[343-65-7]*, $C_{10}H_{12}N_2O_3$, and 3-hydroxy-DL-kynurenine *[484-78-6]*, and drugs such as warfarin, phenprocoumon, and benzodiazepine derivatives can be separated on BSA as well.

Cellulose Triacetate and Cellulose Derivatives.

Properties and Structure. Cellulose *[9004-34-6]* (qv) and other polysaccharides have long been known to have chiral recognition properties. Cellulose is readily available, inexpensive, and has good chemical stability. Microcrystalline cellulose triacetate *[9012-90-3]* (MCA), which is commercially available, is the product of the heterogeneous acetylation of microcrystalline cellulose (31). Various cellulose ester derivatives supported on macroscopic silica gel are available as hplc columns from Diacel (Diacel Chemical Industries, Ltd., Tokyo, Japan). These columns have good mechanical stability and mobile phases such as hexane–2-propanol or alcohols are used. The mechanism of chiral recognition on cellulose-based phases is unknown, although hydrogen bonding and ligand inclusion play a part in resolution (32,33) (see CELLULOSE ESTERS).

Applications. MCA is used for the resolution of many classes of chiral drugs. Polar compounds such as amines, amides, imides, esters, and ketones can be resolved (34). A phenyl or a cycloalkyl group near the chiral center seems to improve chiral selectivity. Nonpolar racemates have also been resolved, but charged or dissociating compounds are not retained on MCA. Mobile phases used with MCA columns include ethanol and methanol.

The Diacel columns can be used for the separation of a wide variety of compounds, including aromatic hydrocarbons having hydroxyl groups, carbonyls and sulfoxides, barbiturates, and β-blockers (35,36). There are presently nine different cellulose derivative-based columns produced by Diacel Chemical Industries. The different columns each demonstrate unique selectivities so that a choice of stationary phases is available to accomplish a separation.

Miscellaneous Chiral Chromatographic Techniques. Cyclodextrins are often used as chiral mobile-phase additives in miscellaneous chromatographic techniques as well as for stationary phases for thin-layer chromatography (35,36). Gas chromatography (gc) columns consisting of derivatized cyclodextrins coated on the capillary column wall are also commercially available (Advanced Separation Technologies, Whippany, New Jersey). Chiral analytes that can be vaporized without degradation or racemization are suitable for analysis on the gc columns. Several reviews and books have been published on the various chiral chromatographic methods (35–37).

Biopolymers in Immunology

Biopolymers are employed in many immunological techniques, including the analysis of food, clinical samples, pesticides, and in other areas of analytical chemistry. Immunoassays (qv) are specific, sensitive, relatively easy to perform, and usually inexpensive. For repetitive analyses, immunoassays compare very favorably with many conventional methods in terms of both sensitivity and limits of detection.

Antigens. One condition that must be met for the application of an immunochemical method is that the analyte must be capable of stimulating an immune response leading to the formation of antibodies in the immunized animal. These antibodies can then be isolated and used as highly specific analytical reagents (immunoassays). Analytes that can combine with the corresponding antibodies are called antigens. There are physical and chemical restrictions on the types of analytes that may be used as immunoassay antigens. In general, large, rigid, chemically complex molecules make good antigens. For example, serum albumin, mol wt ca 60,000, is a good antigen because of its large size, complex structure, and good structural stability. Large repeating polymers such as lipids and carbohydrates, make poor antigens as a result of the simplicity of their structure, even though they may have high molecular weights and good structural stability. One molecule having mol wt 750, the smallest molecular mass that has demonstrated antigenic behavior, is *p*-azobenzene-arsonatetrityrosine (38).

A small analyte is not necessarily prevented from analysis by immunoassay, because a small molecule that is linked to a large antigenic molecule forms a new species having a modified surface structure. Small molecules made antigenic in this manner are called haptens. The larger molecule to which they are attached is called the carrier. The immune response to a hapten-carrier complex is actually triggered by two signals; one from the hapten and one from its carrier. This is necessary, otherwise the hapten would provoke an immune response on its own. Even with the dual signal response, the signal triggered by the complex is still hapten-specific because the immune response is in part triggered by the hapten.

Antibodies. Antibodies are proteins, found in many body fluids such as tears, saliva, and urine, that are present in highest concentrations in blood serum. Because antibodies are proteins (qv), they may be characterized by such physical properties as solubility, electrostatic charge, isoelectric point, and molecular weight. The particular proteins which exhibit antibody activity are the immunoglobulins (Ig). The principal immunoglobulin in blood serum is immunoglobulin G (IgG), the structure of which is similar to the other immunoglobins. IgG is a glycoprotein having mol wt 150,000. It has a Y shape (38) and its structure is shown in Figure 4. There are estimated to be approximately 10 million potential combinations of antigen-binding specificities resulting from light- and heavy-chain combinations in the immunoglobulins. The possibility of utilizing all of these combinations as reagents in immunochemical methods is highly interesting though improbable.

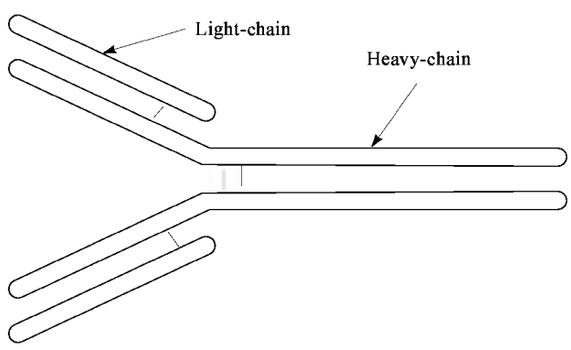


Fig. 4. Simple model of an IgG molecule showing light- and heavy-chain segments where a line (|) between the chains represents a disulfide bond.

General Methodology.

Common Procedures. The general analytical scheme for immunochemical methods is rather simple. The analyte of interest, the antigen (Ag), reacts with the analytical reagent, the corresponding antibody (Ab), forming an immunochemical antigen–antibody complex:

$$Ag + Ab \rightleftharpoons Ag\text{–}Ab$$

The immunochemical interaction between the antigen and antibody is very specific. By labeling either the antigen or antibody, the method's sensitivity is increased. The most frequently used labels to increase sensitivity are radionuclides (see RADIOISOTOPES) where the assay process is called radioimmunoassay (RIA), or enzymes where the assay is named enzyme immunoassay (EIA) (see ENZYME APPLICATIONS).

Labeling. Radioisotopic labeling, one of the first labeling methods used, is still prominent in assays where the use of nonradioisotopic labels

has not been feasible (39). Labeling with enzyme to produce a spectrophotometrically detectable product is frequently used. Fluorescent labeling, used in conjunction with fluorescent polarization detection techniques, can be utilized for small molecules. A commercially available system uses this technique for monitoring drug levels in biological fluids (40). Rare-earth chelates such as those of europium *[7440-53-1]*, Eu, are also successfully used as fluorescent labels (41). The rare-earth chelates have a large Stokes shift that helps to reduce interference from light scattering and from background fluorescence. In addition,these labels have fluorescent lifetimes lasting several hundred microseconds allowing delayed fluorescent sampling.

Chemiluminescent labels, in which the luminescence is generated by a chemical oxidation step, and bioluminescent labels, where the energy for light emission is produced by an enzyme-substrate reaction, are additional labeling types (39,42). Luminol *[521-31-3]*, $C_8H_7N_3O_2$, and acridine *[260-94-6]*, $C_{13}H_9N$, derivatives are often used as chemiluminescent labels.

Variations in Methods. The various immunochemical methods can differ in a number of ways. For example, the analytical reagent may be crude antiserum, monoclonal antibodies, isolated immunoglobulin fractions, etc. The conditions under which the method is run, detection of the antigen–antibody complex, and the techniques used to increase sensitivity or specificity of the reaction all may be varied.

Heterogeneous and Homogeneous Assays. The various immunochemical techniques may be roughly divided into two groups. The first involves homogeneous procedures in which the separation of the bound and free labeled analyte, ie, the radionuclide or the enzyme, is not necessary. In contrast, heterogeneous immunochemical techniques require separation of the bound and free labeled analyte. The most common of these techniques is the enzyme-linked immunosorbent assay (ELISA) (43). In this technique either the antibody or the antigen (analyte) is attached to a solid phase, such as the walls of a polystyrene tube or surface of a plastic bead. Both a competitive and a double antibody (sandwich) ELISA technique are available for measuring antigens.

Sandwich Assays. In the sandwich technique, the most widely used ELISA, the solid surface is first coated with an appropriate antibody as shown in Figure 5. The sample solution containing the antigen (analyte) is then added and allowed to react with the bound antibody on the solid surface. After the reaction any remaining unbound antigens are washed away. Then an enzyme-labeled antibody, specific for a different site on the antigen, is added in a known amount for reaction with the bound antibody–antigen complex. After the reaction any unbound enzyme-labeled antibodies are washed away. A substrate is added which, when acted upon by the bound enzyme, produces a color change the amount of which is a direct measurement of specific enzyme-conjugated bound antibody and therefore of antigen present.

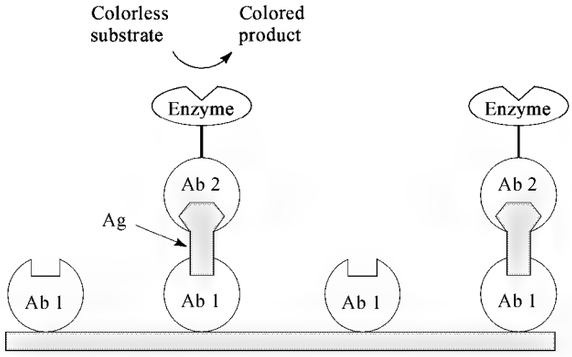


Fig. 5. Scheme of the last steps for the sandwich ELISA. Where Ab 1 represents the the surface-bound antibody, Ag, the antigen, and Ab 2, the enzyme-labeled antibody.

Competitive Assays. The next most widely used type of ELISA is the competitive assay (39,43). In this technique the analyte of interest is mixed with a known amount of enzyme-labeled antigen and both compete for a limited number of binding sites on an antibody that is adsorbed on a solid support. After binding the excess free enzyme-labeled antigen or excess test antigen is washed away. Then a substrate is added which is acted upon by the enzyme-labeled antigen yielding a colored product. The amount of color development is proportional to the amount of enzyme-labeled conjugate bound to the antibody. Little or no color change indicates that the unlabeled antigen of interest was present in the test solution and was bound to the antibody. A color change indicates that enzyme-labeled antigen was bound to the antibody, so that little or no unlabeled antigen was present in the original test solution.

Applications. Immunoassays are used in many different disciplines, having clinical, industrial, agricultural, and environmental applications. This technique has made possible rapid analysis of such varied analytes as viruses, toxins, hormones, foreign proteins, drugs, and insecticides.

As a result of regulations by the Food and Drug Administration, very sensitive and specific analysis techniques have been developed to test for food additives (qv) and possible contaminants in food, many of which are immunochemical methods. For example, botulism toxin and staphylococcal enterotoxins can be detected by ELISA. Animals for slaughter can be quickly screened for diseases such as brucellosis, tuberculosis, and cholera (43). The level of many regulatory enzymes in food can be monitored by immunoassays. Immunoassays are used in beer (qv) brewing to measure the levels of malt enzyme and amyloglucosidase, and in cheese production to measure the level of chymosin, microbial rennets, and beef pepsin *[9001-75-6]* (44). Immunoassays are also useful in the detection of foreign proteins added to foodstuffs. For example, the addition of cheaper meats, such as horse or kangaroo, into beef or pork products can be detected by immunoassays, as well as the inclusion of soybean protein in meat products. Immunochemical methods are often employed to control the production of gluten-free dietary products and hypoallergenic milk. Commercially produced ELISA immuno-kits for food analysis include tests for soya protein (Biokits Ltd., Clwyd, UK), meat species (Biokits Ltd., Clwyd, UK), papain *[9001-73-4]* (Labsystems Oy, Helsinki, Finland), *Salmonella* (Organon Teknika Corp., Durham, North Carolina), trichinosis (Agritech Systems, Portland, Maine; Idetek, San Bruno, California), aflatoxin B_1 *[1162-65-8]*, $C_{17}H_{12}O$, (Neogen Corp., Lansing, Michigan; Agritech Systems, Portland, Maine; Immuno Systems, Biddeford, Maine; Biotech Research Lab, Rockville, Maryland; and Biokits Ltd., Clwyd, UK), aflatoxin M_1 *[6795-23-9]*, $C_{17}H_{12}O_7$, (Neogen Corp., Lansing, Michigan), ochratoxin A (AFRC Food Research Institute, Norwich, UK; Biokits Ltd., Clwyd, UK), atrazine *[1912-24-9]* (Immuno Systems, Biddeford, Maine), antibiotic residues in milk (Angenics Inc., Cambridge, Massachusetts), zearalenone *[17924-92-4]*, $C_{18}H_{22}O_5$, (Neogen Corp., Lansing, Michigan), and *Staphylococcus endotoxun* (Igen, Rockville, Maryland) (45).

Mycotoxins, toxic metabolites of some fungi, can be assayed by immunochemical techniques to determine concentration in animal feed and foodstuffs. Some of the analytes assayed in kits and the detection limits are listed in Table 4 (45). These assays are especially advantageous for routine analysis of large samples of foodstuffs (45,46).

Table 4. Detection Limits of Immunoassays Developed for Mycotoxins and Pesticides

Analyte	CAS Registry Number	Molecular formula	Method	Analyzed food	Detection limit, μg kg[a]
			Mycotoxins		
aflatoxin B_1	*[1162-65-8]*	$C_{17}H_{12}O$	RIA, ELISA	peanuts, cereal	1–5
aflatoxin M_1			RIA, ELISA	milk	0.02–0.1[b]
ochratoxin A	*[303-47-9]*	$C_{20}H_{18}ClNO$	RIA, ELISA	cereals	0.2–2.0

zearalenone	*[17924-92-4]*	$C_{18}H_{22}O_5$	ELISA	cereals	20
			Pesticides		
parathion	*[56-38-2]*	$C_{10}H_{14}NO_5PS$	RIA	lettuce	10
diflubenzuron	*[35367-38-5]*	$C_{14}H_9ClF_2N_2O_2$	ELISA	milk	2
diclofop-methyl	*[51338-27-3]*	$C_1 H_{14}Cl_2O_4$	EIA	sugarbeet, wheat, soybean	100–120
benomyl	*[17804-35-2]*	$C_{14}H_{18}N_4O_3$	RIA	fruit	500

[a] Detection limit is microgram of analyte per kilogram of sample unless otherwise noted.

[b] Units are microgram of analyte per liter of sample.

Immunochemical methods that utilize radioisotopic labeling can detect the use of anabolic sex hormones that increase the growth in meat animals. Stilbene *[588-59-0]*, $C_{14}H_{12}$, trenbolone *[10161-33-8]*, and zeranol *[55331-29-8]*, $C_{18}H_2 O_5$, can be successfully monitored by these immunoassay techniques (45). In order to prevent veterinary drugs from being transported to the human food chain, radioisotopic immunoassays were developed to monitor veterinary antibiotics such as penicillin and chloramphenicol *[56-75-7]*, $C_{11}H_{12}Cl_2N_2O_5$, in meat, milk, and eggs (qv) (see ANTIBIOTICS; MEAT PRODUCTS; MILK AND MILK PRODUCTS).

Pesticide contamination can also be monitored by ELISA. Immunoassays for pesticides are advantageous in that time-consuming sample preparation and purification steps can be avoided or reduced and very high specificity can be obtained in many cases. Various sample kits are available to assay plant tissues, soil, water, and biological fluids. Commercial kits are also available for the determination of atrazine, chlordane *[57-74-9]*, $C_{10}H Cl_8$, heptachlor *[76-44-8]*, $C_{10}H_5Cl_7$, aldicarb *[116-06-3]*, $C_7H_{14}N_2O_2S$, aldicarb sulfone, glyphosate *[1071-83-6]*, $C_3H_8NO_5P$, and chlorpyrifos *[2921-88-2]*, $C_9H_{11}Cl_3NO_3PS$ (47).

Another use of immunoassays is in clinical diagnosis. Biological fluids such as serum and bronchial secretions can be assayed for indications of various disorders, including leukemia, carcinomas, and cancers. Some of the enzymes assayed and the corresponding disorders are listed in Table 5 (44). These assays are based mainly on changes in enzyme concentrations that result from enzyme release from injured tissue or from the changed metabolism of an affected organ. The goal in clinical diagnosis is to develop highly sensitive methods so that symptoms can be detected at the earliest possible stage.

Table 5. Immunoassays of Enzymes in Clinical Diagnosis

Enzyme	Assayed medium	Detected disorder(s)
plasmin	serum	acute leukemia
pepsin, pepsinogen	serum	stomach ulcer, cancer, chronical gastritis
aspartate aminotransferase	serum	infarction, hepatitis
trypsin	serum	acute pancreatitis
pancreatic elastase	serum	pulmonar emphysema, acute pancreatic necrosis, arteriosclerosis
microbial elastase	bronchial secretions	chronical lung infections
acid phosphatase	serum	prostatic cancer
cystein proteinase	tumor medium	breast tumor
ribonuclease	serum	malignant diseases, renal failure
superoxide dismutase		lung cancer
glutamate-oxalacetate transferase	serum	differentiation of chronic liver disease
L-lactate dehydrogenase	serum	differentiation of heart cell damage

Biopolymers as Biosensors

Selectivity is an important consideration in analytical chemistry. Biologically derived polymers can be used as highly selective immobilized reagents in analytical applications. The first reported use of immobilized biopolymers as biosensors (qv) for the detection of an analyte was made in 1962 (48). Since that first reported use there has been a great deal of development and application of immobilized biopolymers in analytical chemistry.

Immobilized Enzymes. The immobilized enzyme electrode is the most common immobilized biopolymer sensor, consisting of a thin layer of enzyme immobilized on the surface of an electrochemical sensor as shown in Figure 6. The enzyme catalyzes a reaction that converts the target substrate into a product that is detected electrochemically. The advantages of immobilized enzyme electrodes include minimal pretreatment of the sample matrix, small sample volume, and the recovery of the enzyme for repeated use (49). Several reviews and books have been published on immobilized enzyme electrodes (50–52).

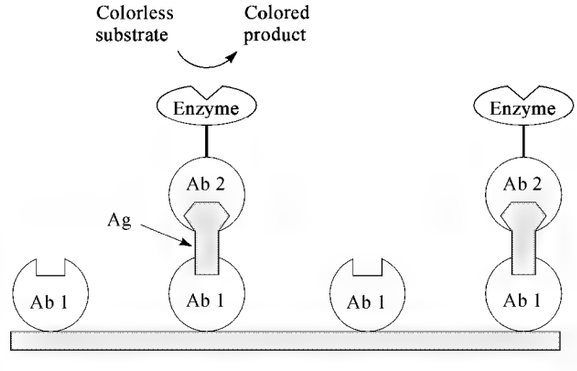


Fig. 6. Diagram of an immobilized enzyme electrode, where S is the substrate and P is the enzyme-bound substrate product.

The enzyme can be immobilized on the electrode by several techniques (53). The simplest method, first used in 1962, is to trap an enzyme solution between the electrode surface and a semipermeable membrane. Another technique is to immobilize the enzyme in a polymer gel such as polyacrylamide which is coated on the electrode surface. Very thin-membrane films can be obtained by electropolymerization techniques (49,54,55) using polypyrrole, polyindole, or polyphenylenediamine films, among others. These thin films (qv) offer the advantage of improved diffusion of substrate and product that

improves the response time. The enzyme can also be covalently bound to the electrode surface either directly or by using a small linking molecule (56). Covalent immobilization has the advantage of improving the stability of the enzyme (57).

The response of the immobilized enzyme electrode can be made independent of the enzyme concentration by using a large excess of enzyme at the electrode surface. The electrode response is limited by the mass transport of the substrate. Using an excess of enzyme often results in longer electrode lifetimes, increased linear range, reduced susceptibility to pH, temperature, and interfering species (58,59). At low enzyme concentrations the electrode response is governed by the kinetics of the enzyme reaction.

Gas-Sensing Enzyme Electrodes. Potentiometry and amperometry are the most common electrochemical techniques to employ enzyme electrodes. Potentiometric gas-sensing and ion-selective electrodes have been converted into enzyme electrodes and used in various analytical applications (53). The gas-sensing electrodes for carbon dioxide and ammonia are most frequently converted to enzyme electrodes because of the lack of response to any dissolved ionic interferents. Decarboxylating or deaminating enzymes are immobilized to these gas-sensing electrodes so that the enzyme reaction product, CO_2 or NH_3, is detected. These potentiometric immobilized enzyme sensors are highly selective and are used for the detection of urea, creatinine, uric acid, amino acids (qv), and nucleotides, as well as other compounds (50,53). Amperometric electrodes are generally coupled with oxidase or dehydrogenase enzymes. Oxidase enzymes can be immobilized on a Clark oxygen electrode and used to detect the amount of oxygen consumed in the enzyme reaction. For example, in the determination of creatinine in blood serum, the enzymes creatinine amidohydrolase, creatine amidinohydrolase, and sarcosine oxidase are coimmobilized on the polypropylene membrane of a Clark oxygen electrode (60). The enzymes catalyze the decomposition of creatinine with the consumption of oxygen, which is monitored by the Clark electrode. The oxidase enzymes can also be trapped on a platinum electrode and used to measure the amount of hydrogen peroxide produced in the enzyme reaction. For example, glucose oxidase *[9001-37-0]* covalently attached to platinum wire via glutaraldehyde *[111-30-8]*, $C_5H_8O_2$, was used to determine glucose *[50-99-7]*, $C_6H_{12}O_6$, levels by monitoring the amount of hydrogen peroxide formed (56). Dehydrogenase enzymes immobilized on glassy carbon or platinum electrodes are used to measure nicotinamide NADH or electron-transfer mediators such as ferrocyanide (53,60). Amperometric immobilized enzyme electrodes are used in the determination of glucose and other sugars, amino acids, cholesterol *[57-88-5]*, $C_{27}H_{46}O$, creatinine, uric acid, and alcohols (53,60).

Multienzyme Electrodes. Coupling the reactions of two or more immobilized enzymes increases the number of analytes that can be measured. An electro-inactive component can be converted by an enzyme to a substrate that is subsequently converted by a second enzyme to form a detectable end product (57). For example, a maltose *[69-79-4]*, $C_{12}H_{22}O_{11}$, sensor uses the enzymes glucoamylase and glucose oxidase, which convert maltose to glucose and then to gluconic acid *[526-95-4]*, $C_6H_{12}O_7$, with the production of hydrogen peroxide, which is detected using a platinum anode (53).

Multienzyme electrodes can increase sensitivity from micromolar to nanomolar detection levels (53,57). In this case the substrate is converted to a detectable product by one enzyme, then that product is recycled into the initial substrate by another enzyme resulting in an amplification of the response signal. For example, using lactate oxidase and lactate dehydrogenase immobilized in poly(vinyl chloride), an amplification of 250 was obtained for the detection of lactate (61).

Miscellaneous Biopolymeric Electrodes. Whereas immobilized enzyme electrodes are most commonly used in electrochemical systems, other types of biopolymers are also employed. For example, a catalytic biosensor uses immobilized antibodies capable of catalyzing chemical reactions (62). In this case, acidic products formed by the catalytic antibody are then detected electrochemically. A micro-pH electrode is used and the catalytic antibody is immobilized in a porous membrane. Biopolymers are also used as semipermeable electrode coatings. This use of biopolymers rejects undesired interferents from the electrode-sensing surface while allowing the transport of the analyte. For example, cellulose acetate is used in this manner as a size-discrimination coating for electrodes (63,64). Lipid coatings prevent polar electroactive compounds from reaching the electrode-sensing surface while letting hydrophobic substances pass through. Cast films of palmitic or stearic acids (65,66) and phosphatidylcholine (67,68) are also used for this purpose. A mixed lipid layer consisting of phosphatidylcholine and cholesterol has improved mechanical stability as well as permeable selective properties (61).

Enzyme Immunosensors. Enzyme immunosensors are enzyme immunoassays coupled with electrochemical sensors. These sensors (qv) require multiple steps for analyte determination, and either sandwich assays or competitive binding assays may be used. Both of these assays use antibodies for the analyte of interest attached to a membrane on the surface of an electrochemical sensor. In the sandwich assay type, the membrane-bound antibody binds the sample antigen, which in turn binds another antibody that is enzyme-labeled. This immunosensor is then placed in a solution containing the substrate for the labeling enzyme and the rate of product formation is measured electrochemically. The rate of the reaction is proportional to the amount of bound enzyme and thus to the amount of the analyte antigen. The sandwich assay can be used only with antigens capable of binding two different antibodies simultaneously (53).

In the competitive binding assay, sample antigen competes with enzyme-labeled antigen for the antibody binding sites on the membrane. The immunosensor is then placed in a solution containing the substrate for the labeling enzyme and the rate of reaction is measured electrochemically. The reaction rate is inversely proportional to the concentration of the sample antigen. This approach is applicable to many analytes including small hapten molecules such as therapeutic drugs.

Enzyme immunosensors are employed for the determination of Hepatitis B surface antigen, IgG, alpha-fetoprotein, estradiol, theophylline, insulin *[9004-10-8]*, and albumin (69,70). However, these immunosensors generally have slow response times and slow reversibility (57).

Enzyme immunosensors are used in flow injection systems and liquid chromatography to provide automated on-line analyses (71–73). These systems are capable of continuously executing the steps involved in the immunoassays, including the binding reactions, washing, and the enzyme reaction, in about 10 minutes.

Economic Aspects

Enantiomeric separations are expected to continue to have a considerable economic impact on the development of new drugs and therapy in the biomedical field. The Food and Drug Administration (FDA) has issued a set of guidelines on New Drug Applications in which the question of stereochemistry was approached directly for the manufacturing of drug substances (74). As of 1987, the FDA requires knowledge of the molecular structure of the drug substance. For chiral compounds this includes identification of all chiral centers. Whereas FDA guidelines do not discuss conditions under which a determination of absolute configuration is essential, it would be appropriate for supporting the manufacture of optically pure drugs (75). These requirements have led to a rapid growth in techniques that measure optical purity of drug substances. Listed in Table 6 are 1991 prices and manufacturers of chiral columns.

Table 6. Chiral Stationary Phases, Manufacturers, and Prices

Stationary phase	Manufacturer	Price[a], $
CYCLOBOND I, β-cyclodextrin	Advanced Separation Technologies Whippany, N.J.	425
CHIRAL-AGP, α_1-acid glycoprotein	Chrom Tech AB Norsburg, Sweden	1100
Enantiopac AGP, α_1-acid glycoprotein	LKB Products Bromma, Sweden	
RESOLVOSIL-BSA, bovine serum albumin	Macherey Nagel Germany	925
CHIRACEL-O series, cellulose	Diacel Chemical Industries Tokyo, Japan	1080

derivatives

[a] Prices are from 1991 catalogs.

The importance of immunoassays for food monitoring and in the detection of diseases is expected to continue to grow as techniques and detection limits improve. In 1991, prices for most immunoassay kits ranged from $250 to $800 depending on the specific kit.

The development of biosensors is expected to benefit monitoring therapeutic drug levels, office testing, and implantable devices because of the advantages of cost-saving automation and data handling. A number of enzyme-based electrodes are commercially available and their manufacturers are given (69). Biosensors are expected to become the predominant sensor technology by the year 2000. The largest market for biosensors is expected to be in clinical laboratories and drug monitoring (76) (see AUTOMATED INSTRUMENTATION CLINICAL CHEMISTRY).

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BIOREACTORS.

See FERMENTATION; REACTOR TECHNOLOGY.

BIOSENSORS

The detection of trace and low levels of biologically active substances is among the most significant and challenging analytical technologies (see TRACE AND RESIDUE ANALYSIS). Devices that enable accurate determination of low concentrations of biologically important compounds have far reaching applications in the fields of medicine, ecology, food science, biotechnology, and military science. Many detection methods employ chemical systems derived directly from biological organisms. Any discrete sensing device that relies on a biologically derived component as an integral part of its detection mechanism is known as a biosensor (see BIOPOLYMERS, ANALYTICAL TECHNIQUES).

Basic Components

All biosensors are composed of two basic parts, the molecular recognition component and the transducer component. The molecular recognition component is typically a complex chemical system usually extracted or derived directly from a biological organism. The function of the molecular recognition component is to interact specifically with a target compound, ie, the chemical to be detected. The molecular recognition component must be capable of discerning the presence of a target in a solution containing possibly hundreds of other compounds, some of which may have molecular structures closely resembling that of the target. The term selectivity is used to quantify the degree to which a molecular recognition system responds specifically to a target while rejecting compounds having related molecular structures. There are three principal classes of molecular recognition components used in biosensors: enzymes or catalytic proteins (qv); immunoglobins, which are biological macromolecules that selectively bind to foreign substances invading an organism; and chemoreceptors, biomolecular units responsible for sensory reception in living organisms (see ENZYME APPLICATIONS). Each class has advantages and disadvantages, and each class comprises a vast number of highly selective possible molecular recognition components.

Once the molecular recognition component interacts with its target, a user-readable signal must be generated. This is the purpose of the transducer component. Ideally, the generated signal should not only report the presence of target but should also relay information concerning the amount or concentration of target compound in the test solution. As of this writing, there were four main types of analytical transducer components employed in biosensors: optical, electrochemical, field effect transistor, and piezoelectric.

The term sensitivity is used to quantify the ability of a biosensor to reliably report target level. There are two separate uses of the term. First, the detection limit of a biosensor is the lowest concentration of target for which the biosensor provides a reliable, reproducible, and unambiguous response. Increasing the sensitivity of a biosensor frequently refers to decreasing the biosensor's detection limit. Second, sensitivity can also refer to the smallest change in concentration from some nominal level of target compound that the biosensor can unambiguously report. Increasing sensitivity in these latter terms is usually a more difficult task than decreasing the detection limit. Herein sensitivity relates to determining differences in concentration. Detection limit is considered as a separate parameter.

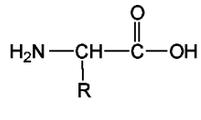
Biosensor design involves consideration of many factors. Molecular recognition components are frequently large complex biomolecules or biological macroassemblies and usually perform efficiently within narrow ranges of pH, temperature, and ionic strength. Degradation and the limited lifetimes of biologically derived components can be important. Additionally, immobilization of enzymes sometimes results in decreased target activity. Factors influencing the selection of an appropriate transducer component include compatibility with the molecular recognition component and the environment in which the biosensor is to be used. Development and optimization of biosensor techniques is a rapidly growing research area; as of the early 1990s, publications on fundamental and applied aspects of biosensing were appearing at a rate approaching 400 papers per year.

Biosensors Based on Chemoreceptors

Chemoreceptors, complex biomolecular macroassemblies, are responsible in part for an organism's ability to sense chemicals in its environment. Most organisms rely heavily on trace level chemical detection to identify food, locate a mate, and sense danger. Chemoreceptors are quite common in biology and can be found in taste buds and the olfactory system. In a biological organism, arrays of highly selective chemoreceptors are employed in chemical sensing. A hound dog, for example, is not only capable of sensing trace amounts of chemicals from dead cells shed from a person to be tracked, but the dog can actually identify the individual from which the cells came. Chemoreceptors are also involved in neural communications and a variety of other nonsensory mechanisms. For example, hormones (qv) are chemical messengers that are sometimes used to trigger organ membranes to change permeability properties by binding to a chemoreceptor located in the membrane. Chemoreceptors have high selectivity, making them excellent candidates for use in biosensors.

Although the integration of complex chemoreceptor arrays, such as those of the olfactory system, into biosensors remains a challenge, research into the use of single chemoreceptors is well underway (1–8). Entire chemoreceptor-containing membranes dissected directly from certain crustaceans have been incorporated. The use of intact structures has the advantage of relatively easy preparation. These materials are readily available and are in an optimal state for molecular recognition. In addition, intact receptor assemblies have been evolved for precisely the purpose of detecting trace chemicals in solution.

In one biosensor design, the chemoreceptive nerve fibers of the antennules of the blue crab *Callinectes sapidus* are connected to a micropipet electrode. This assembly has been termed a receptrode (2). The receptrode created from *Callinectes sapidus* responds to the presence of amino acids (1) (qv) in concentrations as low as 10^{-9} M.



(1)

Moreover, the receptrode has an extremely rapid response time, requiring only two to three milliseconds to fully respond to a target concentration change. The response times of conventional chemical sensors (qv) are typically from several seconds to several minutes. The receptrode exhibits a response that follows the empirical relationship

$$R = \frac{R_{max}}{\left[1 + \left(\frac{K}{C}\right)^{n}\right]}$$

where R_{max} is the maximum observed response, K is the equilibrium constant for the binding of the amino acid to the chemoreceptor, C is the molar concentration of target amino acid, and n is the cooperativity coefficient, a constant included to compensate for differences in sensitivity between different receptors.

This relationship is very similar to the Michaelis-Menton equation commonly used in enzyme kinetics. Interestingly, this receptrode is sensitive within a much wider range of target concentrations than that predicted by Michaelis-Menton kinetics possibly because the crab aesthestasc, hairlike structures in the antennule that contains the chemoreceptors, is actually a chemoreceptor array with up to 500 distinct receptors having different detection limits. The living blue crab is known to detect amino acid concentrations of 10^{-15} M, six orders of magnitude better than the detection limit of the biosensor created from the same antennule because the transducer component of the receptrode biosensor is a single-micropipet electrode and cannot take full advantage of the extremely low detection limits afforded by the receptor array. Similar biosensors that detect hormones, nucleotides, drugs, and toxins, using chemoreceptor-based molecular recognition components extracted from crayfish, lobster, and catfish, have also been created (5,6).

Chemoreceptors have also been isolated from sensory organs, purified, and used as molecular recognition components in biosensors. A biosensor is being developed to detect low levels of the neurotransmitter acetylcholine *[51-84-3]*, $C_7H_{15}NO_2$, (2) (7). The biosensor comprises an acetylcholine receptor-containing lipid membrane coupled to an ion-sensitive field effect transistor (ISFET). An ISFET is a semiconductor device that has a channel below it and is insulated from a gate above it (see SEMICONDUCTORS). On either side of the channel are layers of *n*-type silicon, one called the source, the other the drain. Electrical conduction in the channel is related to changes in the electric field above the gate, which is in turn very sensitive to the ionic strength of a solution in contact with the gate. A schematic of a chemoreceptor-modified ISFET biosensor is shown in Figure 1. In this biosensor application, the receptor-impregnated membrane, extracted from the electric fish *Torpedo Californica*, is purified and coated onto the gate of the transistor. On binding acetylcholine, the local ionic strength of the solution in the vicinity of the chemoreceptor membrane increases. Consequently, the source-drain current in the ISFET increases. Changes in source-drain current are easily detected by a simple ammeter and can be related to the concentration of acetylcholine in the test solution. Micromolar quantities of acetylcholine are utilized.

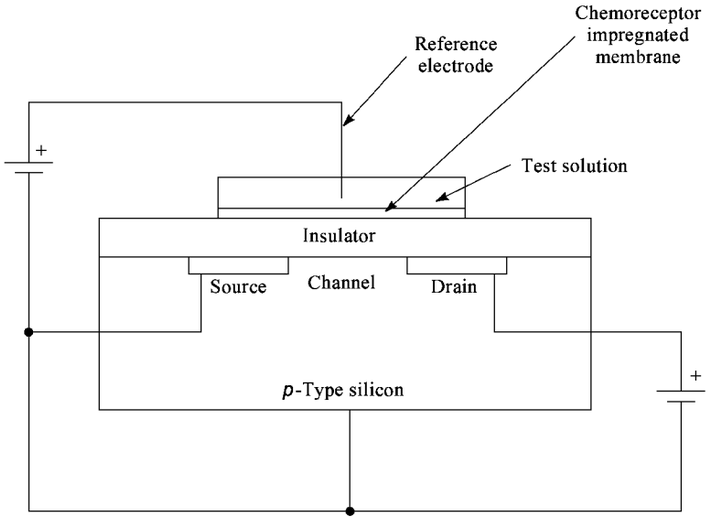
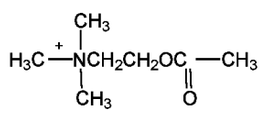


Fig. 1. Schematic for chemoreceptor-modified ISFET biosensor for detection of acetylcholine where the source and drain are both *n*-type silicon.



(2)

The low detection limit, high sensitivity, and fast response times of chemoreceptor-based biosensors result primarily from the extremely high binding constants of the receptor R for the target substrate S. The receptor–substrate binding may be described

$$R + S \rightleftharpoons R\text{–}S$$

where R–S is the bound receptor–substrate complex.

The binding constant is defined by the equilibrium constant for the reaction

$$K = \frac{[R\text{–}S]}{[R]\,[S]}$$

where the square brackets denote molar concentrations.

Receptor–substrate-binding constants are typically between 10^9 and 10^{12} M^{-1}, at equimolar ratios, implying that when a receptor–substrate complex forms, only one ten-thousandth of one percent of substrate molecules remain unbound.

As of this writing chemoreceptor-based biosensors are not yet on the commercial market. Only a few chemoreceptors have been isolated and their substrates identified. Moreover, those chemoreceptors that have been isolated are fragile and have limited lifetimes.

Biocatalytic Biosensors

In a biocatalytic biosensor the molecular recognition component is an enzyme. Enzymes, macromolecular catalysts that are manufactured by plants and animals, affect the rates of biochemical reactions. Virtually all of the millions of chemical reactions involved in life processes have associated enzymes controlling the rates. Collectively, there are several thousand enzymes known and perhaps many thousand more yet to be discovered.

Enzymes are basically specialty proteins (qv) and consist of amino acids, the exact sequence of which determines the enzyme structure and function. Although enzyme molecules are typically very large, most of the chemistry involving the enzyme takes place in a relatively small region known as the active site. In an enzyme-catalyzed reaction, binding occurs at the active site to one of the molecules involved. This molecule is called the substrate. Enzymes are

highly selective, although most enzymes can be fooled into binding molecules having structures closely resembling that of the substrate. Enzyme–substrate binding has often been thought of as being analogous to a lock and key. Where every lock has a specific key that opens it, every enzyme has a specific substrate to which it binds. Once the substrate has undergone conversion to the reaction product, the active site is freed and is ready to participate in another substrate binding.

The high selectivity of enzymes for their substrates is exploited in numerous ways for use in biosensors. In the simplest type of biocatalytic biosensor, an example of which is shown in Figure 2, enzyme molecules are immobilized onto the surface of an electrode. The electrochemical potential of the enzyme-modified electrode is monitored as the electrode is placed in a test solution. If the test solution contains the target compound, ie, the enzyme's substrate, the electrode potential changes. The magnitude of the change is related to the concentration of target in the test solution. Such enzyme-modified electrodes are only useful for enzymes that catalyze oxidation-reduction (redox) reactions or change solution pH. Table 1 lists some common redox enzymes, their substrates, and their potential for use in biosensing.

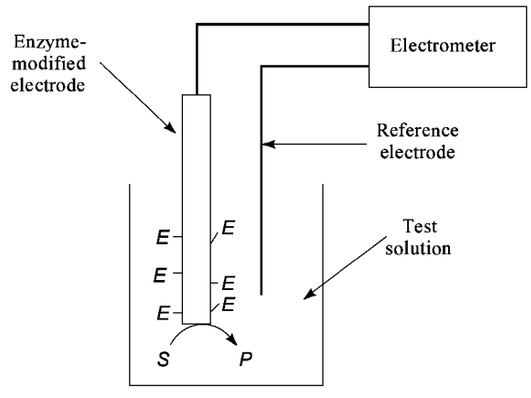


Fig. 2. Schematic of an electrochemical biocatalytic biosensor showing enzyme *E* immobilized onto the electrode where *S* is the substrate (target) and *P* is the product of the enzyme–substrate reaction.

Table 1. Redox Enzymes, Substrates, and Biosensing Potential

Enzyme	CAS Registry Number	Substrate	Potential usage
lactate dehydrogenase	*[9001-60-9]*	lactate	test for metabolic acidosis
D-β-hydroxybutyrate dehydrogenase	*[9001-55-2]*	β-hydroxybutyrate	diabetes testing
glyceraldehyde-3-phosphate dehydrogenase		glyceraldehyde-3-phosphate	test for glycolysis
alcohol dehydrogenase		ethanol	blood alcohol testing
glucose-6-phosphate dehydrogenase	*[9001-40-5]*	glucose-6-phosphate (link to glucose)	diabetes testing
malate dehydrogenase	*[9001-64-3]*	L-malate	test for citric acid cycle
glycerol-1-phosphate dehydrogenase		glycerol-1-phosphate (link to triglycerides)	triglyceride testing
L-glutamate dehydrogenase		L-glutamate	test for citric acid cycle
6-phosphogluconate dehydrogenase	*[9001-82-5]*	6-phosphogluconate	test for pentose phosphate
isocitrate dehydrogenase	*[9001-58-5]*	L-isocitrate	test for citric acid cycle
monoamine oxidase	*[9001-66-5]*	monoamine	drug testing, neurotransmitters, amphetamine, cocaine

Another potential use of redox enzymes in biosensing involves the conversion of enzymes from electrical insulators to electrical conductors (8–12). An electrically conductive redox enzyme is expected to have greatly enhanced efficacy in electrochemically transduced biosensors. In the native, ie, unmodified, enzyme the active site is generally surrounded by insulating polypeptide regions, representing a formidable barrier to electron transfer from the enzyme to the electrode. Chemical modification of these protein regions can, however, render the regions conductive, imparting facile electrical accessibility to the active site. A typical modification involves the covalent bonding of redox moieties to several sites on the enzyme, usually at the lysine residues. Glucose oxidase *[9001-37-0]*, for example, has been modified using ferrocene *[101-54-5]*, $C_{10}H_{10}Fe$, groups, which act as electron relays, mediating conduction to the electrode. Another approach has become known as electrical wiring of redox enzymes. In this method, the redox enzyme is electrostatically complexed to a synthetic polymer that contains a high concentration of redox sites. The polymer provides a conduction pathway or molecular wire between the enzyme and the electrode.

The simple cases where one enzyme is employed afford a limited scope of potential targets. Usually two or more enzyme reactions are coupled, as exemplified by the development of a piezoelectrically-transduced biocatalytic biosensor that couples two enzyme reactions to detect glucose *[492-62-6]*, $C H_{12}O$, (3) (13). In this biosensor a quartz radio crystal is functionalized with the enzyme glucose-6-phosphate dehydrogenase. As shown in Figure 3, a thin film of Prussian blue *[14038-43-8]*, $C_{18}N_{18}Fe_7$, is then coated onto the crystal.

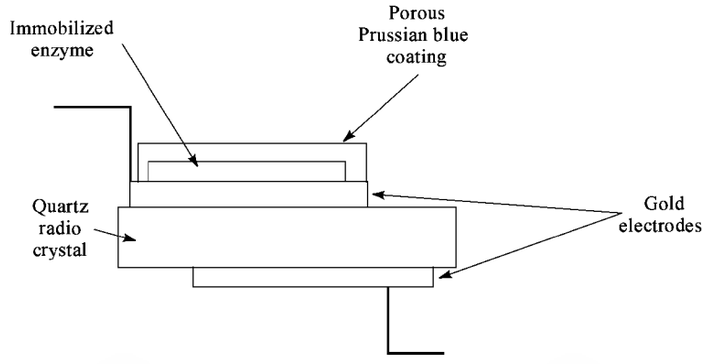


Fig. 3. Detail of enzyme-modified quartz radio crystal used in a piezoelectric biocatalytic biosensor.

The resonant frequency of the crystal is inversely proportional to the mass of the Prussian blue coating. When the immobilized enzyme acts on its substrate, glucose-6-phosphate *[54010-71-8]*, $C_6H_{11}O_9P$, (4), electrons are transferred to the Prussian blue. In order to maintain electrical neutrality, cations such as K^+ or Na^+ present in the test solution are taken up by the Prussian blue film, resulting in an increased film mass that can easily be detected as a frequency change in the radio crystal (Fig. 4). In practice, a second enzyme, hexokinase *[9001-50-8]* is added to the test solution. Hexokinase forms glucose-6-phosphate from glucose. Hence, the target is glucose. This biosensor has a detection limit of approximately 10 μM glucose, and it is highly selective. Unfortunately, the response times are on the order of several minutes because of the slow diffusion rates of the cations into the Prussian blue film.

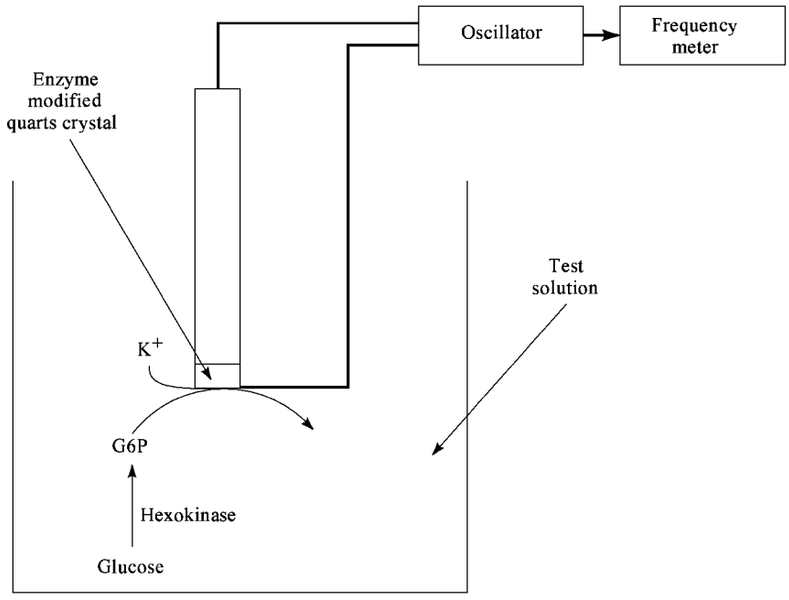
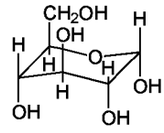
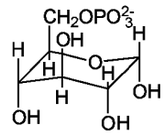


Fig. 4. Schematic of a multisequence biosensor in which the target glucose is first converted to glucose-6-phosphate, G6P, in the test solution by hexokinase. G6P then reacts selectively with glucose-6-phosphate dehydrogenase immobilized on the quartz crystal surface. Electrons released in the reaction then chemically reduce the Prussian blue film (see Fig. 3), forcing an uptake of potassium ions. The resulting mass increase is manifested as a frequency change in the crystal.



(3)



(4)

Several biocatalytic biosensors employing optical transducer components have also been developed (14). One ingenious design for the detection of glucose (15,16) involves immobilization of the enzyme glucose oxidase *[9001-37-0]* onto the end of an optical fiber, along with a fluorescent dye such as pyrenebutyric acid *[3443-45-6]*, $C_{20}H_{1}O_2$, or perylenedibutyrate *[93838-72-3]*, $C_{28}H_{24}O_4$. Glucose oxidase selectively catalyses the reaction of glucose to gluconic acid *[526-95-4]*, $C_6H_{12}O_7$.

$$\text{glucose} + O_2 \rightarrow \text{gluconic acid} + H_2O_2$$

The dye is excited by light supplied through the optical fiber (see FIBER OPTICS), and its fluorescence monitored, also via the optical fiber. Because molecular oxygen, O_2, quenches the fluorescence of the dyes employed, the intensity of the fluorescence is related to the concentration of O_2 at the surface of the optical fiber. Any glucose present in the test solution reduces the local O_2 concentration because of the immobilized enzyme resulting in an increase in fluorescence intensity. This biosensor has a detection limit for glucose of approximately 100 μ*M*; response times are on the order of a minute.

Several other biosensors have been developed using this oxygen-quenched fluorescence approach. Target species include ethanol *[64-17-5]*, C_2H O, hydrogen peroxide *[7722-84-1]*, H_2O_2, lactate, and xanthine *[69-89-6]*, $C_5H_4N_4O_2$, using alcohol oxidase, catalase *[9001-05-2]*, lactate oxidase, and xanthine oxidase, respectively. An additional technique for biocatalytic biosensors involves the firefly chemiluminescent reaction (17):

$$\text{ATP} + \text{luciferin} + O_2 \rightarrow \text{AMP} + \text{oxiluciferin} + CO_2 + \text{pyrophosphate} + \text{light}$$

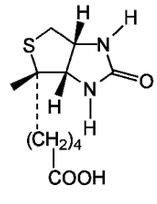
Adenosine triphosphate *[56-65-5]* (ATP) and adenosine monophosphate *[16955-44-5]* (AMP) are relatively small biomolecules common to all organisms and are readily available. Luciferin is a biomolecule extracted from firefly lanterns. This reaction is catalyzed by the enzyme luciferase, also extracted from firefly lanterns. A biosensor has been developed in which luciferase is immobilized onto the tip of an optical fiber, which is immersed in test solution. Luciferin is then added to the test solution. The target is ATP. Any ATP in the test solution catalyzes the chemiluminescent reaction at the tip of the optical fiber. Through the use of photon counting techniques, ATP concentrations as low as 2.8×10^{-10} *M* can be detected. This scheme may prove very promising for the future of biosensors, because ATP is a cofactor in many biochemical processes. In addition, ATP is produced or consumed in numerous enzyme reactions, making this scheme generalizable to a large number of potential targets by enzyme coupling.

Immunological Biosensors

The molecular recognition components of immunological biosensors are antibodies. Antibodies, manufactured when a foreign organism invades an animal's blood, are proteins that constitute part of an animal's immune system. The antibodies bind to and incapacitate the invader and are highly specific. Specific antibodies can be made by injecting an animal, usually a rabbit, with target substance, allowing time for the animal to produce the target-specific antibodies, and then extracting the antibodies from the animal's blood. A substance that produces antibodies when injected in an animal is said to be immunogenic. Antibodies can be made toward bacteria, viruses, fragments of microorganisms, large biomolecules, and even some small organic molecules that have been appropriately derivitized to make them immunogenic. The immunogenic molecule, organism, or fragment that generated the antibody is called the antigen. The isolated antibodies bind the specific antigen toward which they were produced exhibiting extremely high selectivity and forming an antibody–antigen complex (see IMMUNOASSAY).

An electrochemically-transduced immunological biosensor is being developed (18) in which antibodies specific to the Wassermann antigen, produced during a syphilis infection, are immobilized in a cellulose membrane separating two solution compartments. One compartment is coupled to a reference electrode; the other contains test solution. Upon exposure to Wassermann antigen in the test solution, an electrochemical potential change occurs between the two solutions. This change in potential is measured by an electrometer.

Another very clever technique, this one employing monoclonal antibodies, forms the basis of a device being marketed by Molecular Devices Corp., Menlo Park, California. The device is capable of detecting down to attomole (10^{-18} mol) quantities of target protein or polynucleotide (19–23). One application of this technique is as a sensor for DNA. Pharmaceuticals (qv) manufactured using recombinant DNA techniques may consequently contain trace amounts of potentially harmful DNA contaminants. The ability to assay for such contaminants is of paramount importance in the production of safe drugs. The test solution is first incubated with a conjugate of biotin *[58-85-5]*, $C_{10}H_{1}$ N_2O_3S, (5) and single-stranded DNA-binding protein (SSB) extracted from *Escherichia coli.* Any DNA in the test solution is captured by the SSB forming a biotin–SSB–DNA complex. The solution is then incubated with streptavidin, a biomolecule present in *Streptomyces avidinii* that binds biotin with extreme avidity. Biotin, otherwise known as vitamin H, is a growth factor found in every living cell (see VITAMINS, BIOTIN). This latter incubation step forms a streptavidin–biotin–SSB–DNA complex that then reacts with monoclonal anti-DNA antibody complexed to the enzyme urease *[9002-13-5]*. Any DNA in the test solution therefore ultimately forms a streptavidin–biotin–SSB–DNA–anti-DNA–urease complex. The solution is filtered through a biotin-coated nitrocellulose membrane, which binds the streptavidin component of the complex.



(5)

A technique known as light-addressable potentiometric sensor (laps) is then used to assay the presence of the complex by detection of the urease (22). Laps employs a semiconducting silicon wafer in contact with an electrolyte solution through a thin insulating layer. The electrochemical potential of the solution is poised with a controlling electrode. An alternating photocurrent is induced in the system by illumination of the wafer using an intensity modulated light-emitting diode (LED). The conductivity of the insulating barrier, and consequently the photocurrent, is highly sensitive to pH changes in the solution. The nitrocellulose membrane is compressed against the laps device and the complex containing urease, present in the membrane in proportion to the concentration of DNA in the test solution, produces the pH change. This laps DNA sensor has a reported detection limit of 20 pg total DNA. This technique can be generalized to other enzymes producing pH change. The technique is so sensitive that only 600,000 molecules of enzyme are needed to produce a detectable signal.

Under development are biosensors coupling the laps technology with living microorganisms. The metabolic processes of the microorganisms cause pH changes at the surface of the laps wafer. Such biosensors are called microphysiometers or cytosensors. One application of a microphysiometer is directed at replacing the well-known and somewhat controversial Draize test for ocular irritancy, in which compounds are placed in rabbit eyes to test the capacity to irritate (21) (see COSMETICS). A correlation has been found between a compound's ocular irritancy properties and its ability to inhibit metabolism in keratinocytes.

Factors Affecting Biosensor Detection Limits

Biosensor designers are striving for lower detection limits, higher sensitivity, greater selectivity, and lower occurrences of false-positive signals. The detection limit for a biosensor is related to both the nature of the molecular recognition component and the transducer component. In general, antibodies and chemoreceptors are well-suited for low detection limit biosensors because of the high binding constants for target molecules. In intact chemoreceptors the receptor–transducer interface is bridged by a nerve bundle that functions to convert receptor–substrate binding events to electrochemical signals. Whereas the direct output of the chemoreceptor may be quite subtle at trace target levels, it is nevertheless capable of triggering an action potential in the attached nerve. The action potential is an electrical signal, mediated by the motion of ions, that travels along the nerve axon. The action potential produces an electrochemical signal many times larger and thus more easily detectable than the initial trigger.

In general, low level detection is masked by the noise level inherent in any measuring device. Electrochemical methods are susceptible to electrical interference from external sources, variations in reference electrode parameters resulting from aging or contamination, and interference from redox

contaminants in the test solution. Piezoelectric methods measure minute mass and microviscosity changes concurrent with molecular recognition events. These methods are highly susceptible to interference from substances in the test solution that can adsorb to the quartz crystal such as proteins. Optical methods that involve the onset of luminescence on molecular recognition are limited primarily by the detection limits of the biological component. However, those methods in which molecular recognition results in a decrease of luminescence from a nominal level are much less sensitive.

A clever method frequently employed to decrease detection limits in biosensors is enzyme amplification. An example is enzyme multiplied immunoassay technology (emit). In this method antibody is formed for the target compound, isolated, and complexed with the target chemically attached to an enzyme which catalyzes an indicator reaction producing a deeply colored substance. The antibody–antigen–enzyme complex (Ab–T–E) is immobilized in a gel layer on a plastic strip. On exposure to target, competitive binding for the antibody occurs displacing some enzyme-tagged target. The freed enzyme then catalyzes the indicator reaction deeply coloring an area on the strip. Because the enzyme is catalytic, only trace amounts need be released to produce a readable positive.

A variation of this methodology, illustrated in Figure 5, is known as enzyme-linked immunosorbant assay (elisa) (24). Target molecules *T* are covalently attached onto the tip of an optical fiber. Antibody Ab_1 specific to the target is then added to the test solution. Any target in the test solution binds to the antibody. The amount of free, ie, unbound, antibody is then assayed by inserting the fiberoptic probe in the test solution. Free antibody binds to the probe via antibody–antigen complexation with the attached target molecule. The probe is then inserted into another solution containing a second antibody Ab_2 called the detector antibody, which selectively binds the first antibody. The detector antibody is modified with an enzyme that produces a fluorescent compound and the fluorescence is monitored via the fiber-optic.

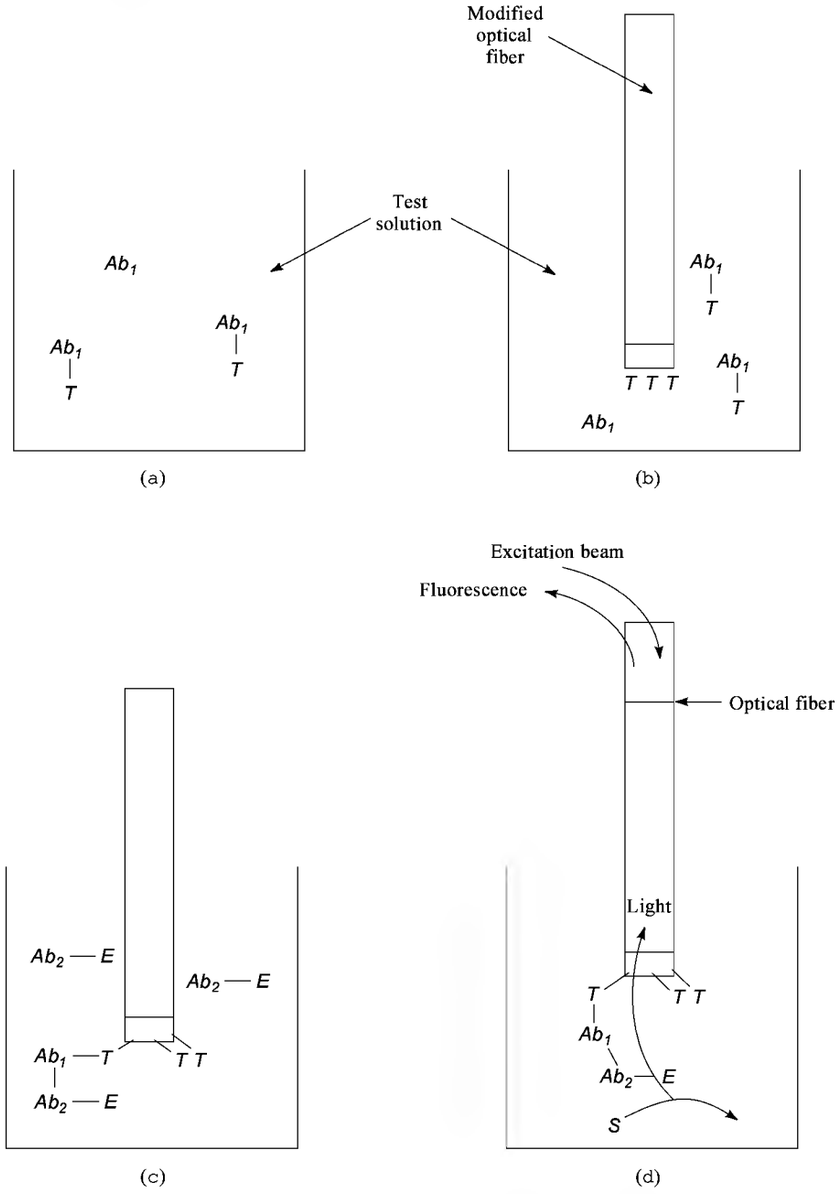


Fig. 5. (**a**) Antibody Ab_1 is added to test solution where some or all of Ab_1 becomes complexed with target, *T*. (**b**) A fiber-optic probe containing covalently attached target is inserted into the solution. Unbound Ab_1 binds to probe. (**c**) The probe is inserted into solution containing enzyme-modified detector antibody Ab_2-*E*, which binds to probe if any Ab_1 is attached. (**d**) The probe is inserted into a solution producing a fluorescent compound, which is then detected via the optical fiber.

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BIOSEPARATIONS.

See BIOPOLYMERS, ANALYTICAL TECHNIQUES.

BIOTECHNOLOGY

This article offers an overview of the coverage of biotechnology, ie, the use of biochemical and biological materials and processes, in the *Encyclopedia.* Biotechnology has long had a role in chemical technology, and information on the various processes and materials is well integrated in articles throughout the *Encyclopedia.*

In the early years of the chemical industry, use of biological agents centered on fermentation (qv) techniques for the production of food products, eg, vinegar (qv), cheeses (see MILK AND MILK PRODUCTS), beer (qv), and of simple organic compounds such as acetone (qv), ethanol (qv), and the butyl alcohols (qv). By the middle of the twentieth century, most simple organic chemicals were produced synthetically. Fermentation was used for food products and for more complex substances such as pharmaceuticals (qv) (see also ANTIBIOTICS). Moreover, supports were developed to immobilize enzymes for use in industrial processes such as the hydrolysis of starch (qv) (see ENZYME APPLICATIONS).

Advances in molecular biology and genetic engineering (qv) during the latter part of the twentieth century have widened the scope of possibilities for the use of biotechnological methods and resulted in increased interest on the part of the chemical industry. Microorganisms and mammalian cells are grown on an industrial scale (see AERATION, BIOTECHNOLOGY; CELL CULTURE TECHNOLOGY) to be harvested for their chemical output (see GROWTH REGULATORS; HORMONES; HUMAN GROWTH FACTOR; INSULIN AND OTHER ANTIDIABETIC DRUGS; and VACCINE TECHNOLOGY). Enzymes and microorganisms are utilized industrially to effect chemical modification of materials or to direct the outcome of synthetic reactions (see ENZYME APPLICATIONS IN ORGANIC SYNTHESIS; MICROBIAL TRANSFORMATIONS). Customized biological molecules are biologically produced to meet the needs of industry (see ENZYME INHIBITORS; IMMUNOTHERAPEUTIC AGENTS; PHARMACEUTICALS; PROTEIN ENGINEERING). Biopolymers (qv), ie, carbohydrates (qv), enzymes, nucleic acids (qv), and proteins (qv), are used in clinical and chemical analyses both for detection (see AUTOMATED INSTRUMENTATION, CLINICAL CHEMISTRY; BIOSENSORS; IMMUNOASSAY; MEDICAL DIAGNOSTIC REAGENTS) and for separation (see BIOPOLYMERS, ANALYTICAL TECHNIQUES; CHROMATOGRAPHY) of materials.

The following is an alphabetized list of articles directly related to biotechnology in the *Encyclopedia.* However, even this list does not embrace all of the discussions of biochemical processing in the *Encyclopedia* because coverage of biotechnology is not limited to the highly specialized products and techniques of this subindustry. Designs appropriate to bioprocesses are also included in many of the unit operations articles (see REACTOR TECHNOLOGY; SEPARATION, CENTRIFUGAL; STERILIZATION; and ULTRAFILTRATION. Also as new developments continually occur, materials articles will have appropriate up-to-date discussions of biotechnological methods.

Aeration, Biotechnology
Automated instrumentation, Clinical chemistry
Automated instrumentation, Hematology
Biopolymers, Survey
Biopolymers, Analytical techniques
Biosensors
Biotechnology
Cell culture technology
Chromatography
Enzyme applications, Industrial
Enzyme applications, Therapeutic
Enzyme applications in organic synthesis
Enzyme, inhibitors
Fermentation
Genetic engineering, Procedures
Genetic engineering, Microbes
Genetic engineering, Plants
Genetic engineering, Animals
Immunoassay
Immunotherapeutic agents
Insulin and other antidiabetic drugs
Medical diagnostic reagents
Microbial polysaccharides
Microbial transformations
Nucleic acids
Protein engineering
Proteins
Vaccine technology
Yeasts

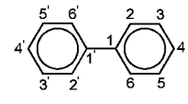
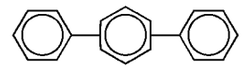
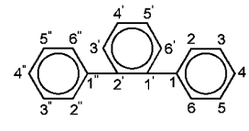
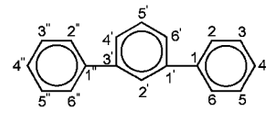
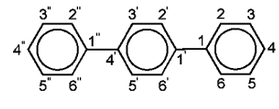
BIOTIN.

See VITAMINS.

BIPHENYL AND TERPHENYLS

Biphenyl (diphenyl, phenylbenzene) and terphenyl are the lowest members of a family of polyphenyls in which benzene rings are attached one to another in a chainlike manner, $C_6H_5(C_6H_4)_mC_6H_5$. Many higher polyphenyls are known (1), but only biphenyl and the terphenyls are of commercial significance. Some lower boiling quaterphenyl isomers, $C_{24}H_{18}$, are sometimes included in products obtained by high vacuum distillation of crude terphenyls. Structures of biphenyl, $C_{12}H_{10}$, and the three terphenyl isomers, $C_{18}H_{14}$, are shown in Table 1.

Table 1. Biphenyl and the Terphenyls

Common name	CAS name	CAS Registry Number	Structure
biphenyl	1,1′-biphenyl	*[92-52-4]*	
	terphenyl	*[26140-60-3]*	
o-terphenyl	1,1′:2′,1″-terphenyl	*[84-15-1]*	
m-terphenyl	1,1′:3′,1″-terphenyl	*[92-06-8]*	
p-terphenyl	1,1′:4′,1″-terphenyl	*[92-94-4]*	

Biphenyl was first reported in 1862 (2) and identified in 1867 (3) as the main product obtained by passing benzene vapors through a hot tube. In a 1874 investigation (4) of the higher boiling products of benzene pyrolysis, benzene vapors were passed through a glowing iron pipe, and, in addition to biphenyl, *m*- and *p*-terphenyl were isolated. The ortho-isomer was identified in 1927 (5). Shortly thereafter, biphenyl and (coincidently) terphenyls became commercially available by a dehydrocondensation process in which benzene vapor was passed through molten lead baths at 750°C (6). Although the lead pots have long since been replaced by modern gas or electrically heated tube reactors, vapor-phase dehydrocondensation of benzene *[71-43-2]* is still an important commercial route to biphenyl; it is the method of choice for production of terphenyls.

Physical Properties

Pure biphenyl is a white crystalline solid that separates from solvents as plates or monoclinic prismatic crystals. Commercial samples are often slightly yellow or tan in color. Similarly, pure terphenyls are white crystalline solids whereas commercial grades are somewhat yellow or tan. Physical and chemical constants for biphenyl and the three isomeric terphenyls are given in Tables 2 and 3, respectively.

Table 2. Physical Properties of Biphenyl

Property	Value	Reference
melting point, °C	69.2	7
freezing point commercial grades, °C	68.5–69.4	8
boiling point at 101.3 kPa[a], °C	255.2 ± 0.2	7
specific gravity, solid		
d^{20}	1.041	9

d^{15}			0.991		9
critical properties					
temperature, °C			515.7		10
pressure, MPa[b]			4.05		10
density, g mL			0.314		10
flash point, °C			113.0		11
fire point, °C			123.0		11
autogenous ignition temperature, °C			560.0		12
heat of combustion, kJ mol[c]			6243.2		13
heat of fusion, kJ mol[c]			18.60		12
	Temperature, °C				
	100°C	200°C	300°C	350°C	
vapor pressure, kPa[a]		25.43	246.8	558.06	9
liquid density, g mL	0.970	0.889	0.801	0.751	9
heat capacity, J g[c]	1.786	2.129	2.468	2.640	9
heat of vaporization, J g[c]	397.0	343.0	284.7	251.0	9
viscosity, mm^2 s (cSt)	0.98	0.43	0.24		11
thermal conductivity liquid, W (cm·K)[d]	13.39	11.92	10.46	9.75	14

[a] To convert kPa to mm Hg, multiply by 7.5.

[b] To convert MPa to psi, multiply by 145.

[c] To convert J to cal, divide by 4.184.

[d] To convert W (cm·K) to (cal·cm) (s·cm^2·°C), divide by 4.184.

Table 3. Physical Properties of Pure Terphenyl Isomers

Property	*Ortho-*	*Meta-*	*Para-*	Reference
melting point, °C	56.2	87.5	212.7	15
boiling point at 101.3 kPa[a], °C	332.0	365.0	376.0	16
heat of vaporization of 101.3 kPa[a] at bp, kJ kg[b]	253.0	279.0	272.0	16
flash point, °C	171.0	206.0	210.0	17
fire point, °C	193.0	229.0	238.0	17
auto ignition temperature, °C	530.0	555.0	555.0	12
vapor pressure, kPa[a]				
93°C	0.01172	0.00165		16
204°C	2.834	0.827		16
315.6°C	64.40	27.3		16
426.7°C	439.9	240.6		16
density of liquid, g L				
93°C	1022.0	1039.0	solid	18
204°C	935.0	958.0	solid	18
315.6°C	842.0	871.0	879.0	18
heat capacity of liquid, kJ kg[b]				
93°C	1.007	0.970		16
315°C	1.300	1.298		16
398.9°C	1.400	1.397	1.116	16
viscosity of liquid, mPa·s (cP)				
100°C	4.34	3.87	solid	19
225°C	0.66	0.78	0.74	19
300°C	0.30	0.40	0.43	19
350°C			0.32	19
thermal conductivity of liquid, W (m·K)[c]				
100°C	0.1316	0.1347		19
150°C	0.1266	0.1306		19
210°C	0.1206	0.1356	0.1359	19
260°C			0.339	19
heat of vaporization, J g at 252°C	280.0	298.0	305.0	20
heat of fusion, kJ kg[b]	55.2	73.7	146.5	
critical temperature, K	891.0	927.0	926.0	19
critical pressure, MPa[d]	3.903	3.503	3.330	21

[a] To convert kPa to mm Hg, multiply by 7.5.

[b] To convert J to cal, divide by 4.184.

[c] To convert W (m·K) to (cal·cm) (s·cm^2·°C), divide by 418.4

[d] To convert MPa to psi, multiply by 145.

Individual terphenyl isomers are not ordinarily isolated in pure form but are most often utilized as isomer mixtures. During the late 1950s and 1960s, terphenyls and partially hydrogenated derivatives, because of their radiation resistance and good thermal stability, were regarded as promising organic coolants for nuclear reactors. Many physical property studies of biphenyl and the terphenyls, both as pure compounds and in various mixtures, were carried out. Extensive collections of physical property data which attest to the high degree of activity engendered by the nuclear application are available (7,12,22). As interest in organic-cooled reactors declined, industrial heat-transfer applications remained the main outlet for terphenyls. Although the latter was served

primarily by partially hydrogenated terphenyl mixtures, Monsanto for many years marketed the unhydrogenated terphenyl precursor having a composition of approximately 2–10% *o*-terphenyl, 45–49% *m*-terphenyl, and 25–35% *p*-terphenyl with 2–18% higher polyphenyls. The product's high liquidus temperature (about 145°C) hampered its utility as a heat-transfer medium. A more useful composition containing less *p*-terphenyl and more low melting quaterphenyls is now commercially available. Some physical properties of this low melting polyphenyl mixture are given in Table 4.

Table 4. Physical Properties of a Commercial[a] Terphenyl–Quaterphenyl Mixture

Property	Value
composition	~65% terphenyls ~45% *ortho*- ~50% *meta*- ~5% *para*- ~35% quaterphenyls
appearance	soft solid melting to yellow liquid
melting range, °C	40–70
flash point, °C[b]	204.0
fire point, °C[b]	232.0
autogenous ignition temperature, °C	538.0
kinematic viscosity, mm^2 s (= cSt) at 50°C	97.9
coefficient of thermal expansion per °C	8.8×10^{-4}
heat of vaporization, J g[c]	
boiling range at 6.66 kPa[d], °C	239
10% over	255.0
90% over	340.0

[a] Monsanto Product Bulletin IC FP-215A, 1990.

[b] Cleveland Open Cup.

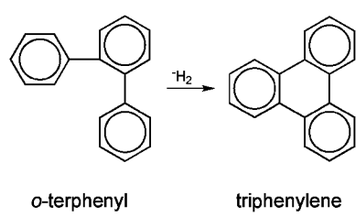
[c] To convert J to cal, divide by 4.184.

[d] To convert kPa to mm Hg, multiply by 7.5.

Chemical Properties

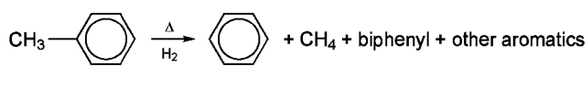
Biphenyl and terphenyls may be regarded as substituted benzenes that undergo acylation, alkylation, halogenation, nitration, sulfonation, and other reactions common to benzene (qv). The points of initial attack on chlorination, nitration, and sulfonation of biphenyl occur at the 2- and 4-positions; the latter predominates. Alkylation by olefins, which affords the most commercially important class of biphenyl derivatives, takes place largely at the 4-position. Alkyl substituents in the 4-position can reorganize under the influence of strong Lewis acids to a mixture of 3- and 4-substituted biphenyls in which the 3-alkyl isomer often predominates (23). Acid catalyzed alkylation of biphenyl can also be effected by alkyl transfer from a polyalkylbenzene. This reaction is most facile when the alkyl group is ethyl (24). Considerable attention has been focused on developing catalysts and conditions for the selective diisopropylation of biphenyl in the 4,4′-positions (25,26). The resulting 4,4′-diisopropylbiphenyl *[18970-30-4]* can be oxidized to the corresponding [1,1′-biphenyl]-4,4′-dicarboxylic acid *[787-70-2]* (27), regarded as a promising monomer for heat-resistant and liquid crystal polymers (28).

Terphenyls, like biphenyl, undergo the usual reactions of aromatic hydrocarbons. The ortho- and para-isomers nitrate initially at the 4-position whereas the meta-isomer nitrates at the 4′-position (29). *Ortho*- and *m*-terphenyl can be isomerized to the para-isomer (30,31). *o*-Terphenyl, refluxed for a short time with aluminum chloride in benzene, gives 94% meta-isomer. More drastic isomerization conditions afford conversions of up to 84% para-isomer. Isomerization in the other direction also can be forced. Japanese workers (32) claim a 29% yield of *o*-terphenyl by slow fractionation of *o*-terphenyl from a 64:36 mixture of *m*- and *p*-terphenyl heated at 530–535°C over a Y-type zeolite catalyst. Currently, isomerizing the more abundant meta- and para-isomers is the more attractive direction, since *o*-terphenyl, because of its low melting point, is the most useful of the three isomers for heat-transfer applications. Commercially, partial reduction to a complex mixture of dicyclohexylbenzenes, biphenylcyclohexanes, and phenyldicyclohexane is the most important reaction that the terphenyls undergo. Under strongly dehydrogenating conditions, *o*-terphenyl cyclizes to triphenylene *[217-59-4]* (33). The latter is a minor (1.5%) impurity present in crude polyphenyls prepared by pyrolytic dehydrocondensation of benzene.



Manufacture

Biphenyl has been produced commercially in the United States since 1926, mainly by The Dow Chemical Co., Monsanto Co., and Sun Oil Co. Currently, Dow, Monsanto, and Koch Chemical Co. are the principal biphenyl producers, with lesser amounts coming from Sybron Corp. and Chemol, Inc. With the exception of Monsanto, the above suppliers recover biphenyl from high boiler fractions that accompany the hydrodealkylation of toluene *[108-88-3]* to benzene (6). Hydrodealkylation of alkylbenzenes, usually toluene, C_7H_8, is an important source of benzene, C_6H_6, in the United States. Numerous hydrodealkylation (HDA) processes have been developed. Most have the common feature that toluene or other alkylbenzene plus hydrogen is passed under pressure through a tubular reactor at high temperature (34). Methane and benzene are the principal products formed. Dealkylation conditions are sufficiently severe to cause some dehydrocondensation of benzene and toluene molecules.



Approximately 1 kg of biphenyl per 100 kg of benzene is produced (6). Because of the large scale, HDA operations provide an ample source of crude biphenyl from which a technical grade of 93–97% purity can be obtained by distillation (35). Zone refining or other crystallization techniques are required to further refine this by-product biphenyl to the >99.9% purity required for heat-transfer applications.

High purity biphenyl is currently produced by Monsanto in the United States and United Kingdom by direct dehydrocondensation of benzene. Terphenyls are also obtained from the higher boiling polyphenyl by-products that accompany the biphenyl (36). Foreign producers making biphenyl and terphenyls by the benzene dehydrocondensation route include Bayer (Germany), Nippon Steel (Japan) and Russia. Industrial production is carried out in gas or electrically heated tubular reactors at 700–800°C. Residence times are on the order of 10–30 seconds. Some control on the ratio of biphenyl to terphenyl can be exercised by adjusting temperature and flow rates and by recycling biphenyl. However, there is little control over the ratio of *ortho*-, *meta*-, and *para*-terphenyl isomers produced.

Since the thermal dehydrocondensation proceeds by a free-radical mechanism (37), various radical-forming promoters like acetone, ethanol, or methanol have been found useful in improving conversion of benzene to condensed polyphenyls. In the commercial dehydrocondensation process, benzene and some biphenyl are separated by distillation and recycled back to the dehydrocondensation step. Pure biphenyl is then collected leaving a polyphenyl residue consisting of approximately 4% *o*-terphenyl, 44% *m*-terphenyl, 25% *p*-terphenyl, 1.5% triphenylene, and 22–27% higher polyphenyl and tars. Distillation of this residue at reduced pressure affords the mixed terphenyl isomers accompanied by a portion of the quaterphenyls present. Depending on intended use, more or less of the quaterphenyl fraction is included with the terphenyl cut.

Batchwise fractional distillation can be used to adjust the ratio of isomers in the mixture. For example, the heat-transfer composition of Table 4 is obtained by collecting all of the *ortho*- some of the *meta*-, and excluding most of the *para*-terphenyl present in the natural mixture. Economics and considerations of melting point depression favor inclusion of lower melting quaterphenyl isomers.

Pure *o*-terphenyl can be obtained by fractional distillation. To obtain high purity *m*- or *p*-terphenyl, the appropriate distillation fraction has to be further purified by recrystallizing, zone refining, or other refining techniques. Currently, little demand exists for pure isomers, and only a mixture is routinely produced. Small amounts of acetone, ethanol, or methanol are used to promote dehydrocondensation, and as a result, minor amounts of methyl- or methylene-substituted polyphenyls accompany the biphenyl and terphenyls produced. For most purposes, the level of such products (<1%) is so small that their presence can be ignored. For applications requiring removal of these alkyl-polyphenyl impurities, an efficient process for their oxidative destruction has been described (38).

Shipping

By-product biphenyl is usually sold as a dye carrier in the molten state in tank truck or tank car lots. Grades of higher purity are also sold in the molten state or as flakes in 22.7 kg bags.

Biphenyl is defined as a toxic chemical under, and subject to, reporting requirements of Section 313 of Title III of the Superfund Amendments and Reauthorization Act (SARA) of 1986 and 40 CFR, Part 372 under the name biphenyl. It is identified as a hazardous chemical under criteria of the OSHA Hazard Communication Standard (29 CFR 1910.1200).

The small amount of mixed terphenyls that are sold as such, are shipped in the form of flaked solids in 22.7 kg multiwall bags. The U.S. freight classification is Plastics, synthetic other than liquid, NOIBN. Like biphenyl, mixed terphenyls fall under the hazardous chemical criteria of the OSHA Hazard Communication Standard (29 CFR 1910.1200).

The terphenyl–quaterphenyl heat-transfer medium (Table 4), sold as Therminol 75 heat-transfer fluid, is shipped in drums, tank car, or tank truck lots. Its U.S. freight classification is Heat-Transfer Media, NOIBN. The material does not require a DOT hazardous material label, but does fall under the hazardous chemical criteria of the OSHA Hazards Communications Standard (19 CFR 1910.1200).

Economic Aspects

Reliable estimates of annual production of biphenyl in the United States are difficult to obtain. The 1990 figure is probably on the order of 16 million kg yr of which about half is derived from hydrodealkylation sources. About 10% of the biphenyl derived from HDA sources is consumed, as 93–95% grade, in textile dye carrier applications. The remainder is used for alkylation or upgraded to >99.9% grades for heat-transfer purposes. Essentially all of the high purity biphenyl produced by dehydrocondensation of benzene is used as alkylation feedstock or is utilized directly in heat-transfer applications.

The actual capacity for biphenyl production in the United States is not reported, but considering the flexibility for recovery from hydrodealkylation sources and a shrinking dye carrier market, production capacity for HDA-grade biphenyl substantially exceeds demand. Requirements for high grade biphenyl dropped precipitously following termination of polychlorinated biphenyl production in 1972. During the ensuing decade, benzene dehydrocondensation plants were downsized, and terphenyls became the primary dehydrocondensation product. More recently, the trend has gradually reversed because of expanding heat-transfer and alkylation markets. In 1988 an expansion of production capability was announced by Monsanto (39).

Biphenyl prices vary widely depending on grade, quantities purchased, and special contract arrangements. In 1991 the U.S. published price for 99.9% biphenyl was $1.40 to $1.63 per kg depending on quantity and packaging (40). Lower purity HDA-grades run roughly half this price.

As in the case of biphenyl, current worldwide production figures for terphenyls are not readily obtainable, but the volume is probably around 6.8–8.2 million kg yr. Currently, most of the terphenyl produced is converted to a partially hydrogenated form. U.S. production of terphenyls has remained steady at several thousand metric tons per year over the past decade. The 1991 small lot price for mixed terphenyls was about $3.89 kg whereas the specially fractionated heat-transfer-grade terphenyl–quaterphenyl mixture sold as Therminol 75 heat-transfer fluid was priced around $6.93 kg. Partially hydrogenated mixed terphenyls were priced in the $6.05–7.48 kg range depending on quantity and grade.

Specifications, Analytical Control, and Storage

Biphenyl, terphenyl, and their alkyl or hydrogenated derivatives generally serve markets where price and performance, rather than composition, is the customer's primary concern. Performance standards for heat-transfer applications are usually set by the fluid supplier. The biphenyl–diphenyl oxide eutectic (26.5% biphenyl, 73.5% DPO) represents a special case. This composition has become a widely recognized standard vapor-phase heat-transfer medium. It is sold throughout the world under various trademarks. In the United States, Dow (Dowtherm A) and Monsanto (Therminol VP-1) are the primary suppliers. Alkylated biphenyls and partially hydrogenated terphenyls serving the dielectric and carbonless copy paper dye solvent markets likewise are sold primarily on the basis of price and performance characteristics jointly agreed on by producer and user.

Because the thermal stability of the materials is generally high, gas–liquid chromatography (glc) is by far the most widely used analytical method employed for analysis and quality control in the manufacture of biphenyl, terphenyls, and their derivatives. In the 1980s, reverse-phase high performance liquid chromatography (hplc) became increasingly useful in the analysis of complex high molecular weight polyphenyl mixtures (41), but it is not routinely employed.

Biphenyl and mixed terphenyls as well as their normally liquid alkyl and partially hydrogenated derivatives are commonly stored in the liquid or molten state. The products are noncorrosive; mild steel equipment usually suffices for handling.

Health and Safety Factors

Although biphenyl and the terphenyls fall under the hazardous chemical criteria of the OSHA Hazard Communications Standard, the products themselves are fairly low in toxicity and do not constitute a serious industrial hazard. Some relevant exposure and toxicity data are summarized in Tables 5 and 6.

Table 5. Toxicological Properties of Biphenyl

Measurement	Value	Reference
Airborne exposure limits		

OSHA PEL	0.2 ppm 8 h TWA	42,43
ACGIH TLV	0.2 ppm 8 h TWA	42,43
Toxicity data		
oral, g kg	rat LD_{50} — 2.4	42
	rat LD_{50} — 3.28, rabbit 2.41	44
dermal, g kg	rabbit LD_{50} = >5.01	42
inhalation, mg L	rat LC_{50} = >0.2	42
eye irritation	(rabbit) 2.8 on a scale of 110	42
skin irritation	(rabbit, 24 h) 0.3 on a scale of 8	42

Table 6. Toxicological Properties of Terphenyls

Measurement	Value	Reference
Airborne exposure limits		
OSHA PEL	ceiling = 1.0 ppm (9 mg m^3)	45,46
ACGIH TLV	ceiling — 0.5 ppm (5 mg m^3)	45,46
Toxicological data		
oral, g kg		
mixed isomers	rat LD_{50} = >5	45
ortho-isomer	rat LD_{50} 1.9	47
meta-isomer	2.4	47
para-isomer	>10	47
dermal, g kg	rabbit LD_{50} >12.5 (mixed isomers)	45
eye irritation	(rabbit 24 h) 0.7 on a scale of 110	45
skin irritation	(rabbit 24 h) 0.0 on a scale of 8	45

Because biphenyl is often transported in the molten state, a moderate fire hazard does exist under these circumstances. Biphenyl, with a flash point of 113°C, has a lower flammability limit of about 0.6% (by volume) at the flash point to an upper limit of 5.8% at 166°C (42). Dust explosions are a hazard when vapors from a hot liquid surface condense in air in a confined space.

Environmental Considerations

The widespread use of biphenyl and methyl-substituted biphenyls as dye carriers (qv) in the textile industry has given rise to significant environmental concern because of the amount released to the environment in wastewater effluent. Although biphenyl and simple alkylbiphenyls are themselves biodegradable (48–50), the prospect of their conversion by chlorination to PCBs in the course of wastewater treatment has been a subject of environmental focus (51–53). Despite the fact that the lower chlorinated biphenyls are also fairly biodegradable (49,54,55) continued environmental concern has resulted in decreased use of biphenyl as a dye carrier (see DYES, ENVIRONMENTAL CHEMISTRY).

Terphenyls in heat-transfer applications are used in relatively smaller quantities with negligible release to the environment. They are sufficiently biodegradable so as not to constitute an environmental threat (56,57). Some properties important for environmental considerations are summarized in Table 7.

Table 7. Properties of Biphenyl and Terphenyls of Environmental Importance

Property	Value	Reference
vapor pressure at 25°C, Pa[a] biphenyl	1.3	
water solubility at 25°C, mol dm^3		
biphenyl	4.57×10^{-5}	58
o-terphenyl	5.38×10^{-6}	58
m-terphenyl	6.65×10^{-6}	58
p-terphenyl	7.80×10^{-6}	58
aeration stripping, 4 h COD[b] reduction, %		
biphenyl	89.0	
biphenyl BOD at 20°C	79.0	
octanol–water partition coefficient, log *P*		
biphenyl	4.1	59
p-terphenyl	6.03	60
biphenyl bioconcentration ratio	438 ± 48	

[a] To convert Pa to mm Hg, multiply by 0.0075.

[b] COD Chemical oxygen demand.

Use

In the past, dye carrier applications consumed a significant portion of the biphenyl produced in the United States with heat transfer being a strong but lower volume outlet. A shift away from biphenyl in textile dyeing during the 1980s and a steady growth in the vapor-phase heat-transfer market has caused a reversal of the earlier market positions. The biphenyl and diphenyl ether eutectic is by far the most important biphenyl outlet into the heat-transfer market. The eutectic is sold throughout the world under various trademarks including Dowtherm A (Dow), Therminol VP-1 and Santotherm VP-1 (Monsanto), Diphyl (Bayer), Thermio (ICI), and Therm S-300 (Nippon Steel). The eutectic has a maximum operating temperature of about 400°C. Vapor pressure at this temperature is about 1.1 MPa (11 atm). In seeking heat-transfer fluids capable of 400°C operation, it is often desirable to employ a liquid-phase medium. The terphenyl and quaterphenyl mixture of Table 4 was designed for this purpose. Other lower melting mixtures containing biphenyl, *o*-terphenyl, and *m*-terphenyl in combination with various phenyl ethers have been proposed (38,61) for high temperature solar heat collection systems.

Derivatives

Historically, polychlorinated biphenyls (PCBs) and to a lesser extent polychlorinated terphenyls (PCTs) were the most important derivatives of the respective polyphenyls. When they came to be recognized as serious environmental contaminants, production ceased in the early 1970s. These products are now of significance primarily because of their environmental aftereffects (62). Much environmental research and governmental regulations stem therefrom (see CHLOROCARBONS AND CHLOROHYDROCARBONS, TOXIC AROMATICS).

Short-chain alkylated biphenyls are the principal biphenyl derivatives in commercial use. They are generally produced by liquid-phase Friedel-Crafts alkylation of biphenyl with ethylene, propylene, or mixed butenes. A series of mixed ethylated biphenyl heat-transfer fluids (trademarked Therm S-600, 700, 800) is marketed by Nippon Steel. A mixed diethylbenzene–ethylbiphenyl heat-transfer fluid is also available from Dow (63). Monoisopropylbiphenyl *[25640-78-2]*, largely as a mixture of meta- and para-isomers is produced by Koch Chemical Co. Monoisopropylbiphenyl (MIPB) was selected by Westinghouse (64,65) as a PCB replacement in capacitors and this is its primary application today. For a time MIPB was also employed as a PCB replacement in pressure sensitive copy paper, but this outlet has since given way to other dye solvents. A similar product consisting of a mixture of *sec*-butylbiphenyl isomers *[38784-93-9]* (66) is currently the favored dye solvent for pressure sensitive copy paper (67) manufactured in the United States.

Domestic production figures for alkylated biphenyls are not readily available, but the volume is probably in the range of 10–14 million kg yr with prices at approximately $1.50 per kg.

Ortho- and *para*-phenylphenols are commercially significant biphenyl derivatives that do not involve biphenyl as a starting material. Both are produced as by-products from the hydrolysis of chlorobenzene *[108-90-7]* with aqueous sodium hydroxide (68). *o*-Phenylphenol, ie, 1,1-biphenyl-2-ol *[90-43-7]*, particularly as its sodium salt, is widely used as a germicide or fungicide. *Para*-phenylphenol *[92-69-3]* with formaldehyde forms a resin used in surface coatings.

Several functionalized biphenyls either are, or show promise of becoming, commercially significant polymer building blocks. Thus new routes to 4,4′-dihydroxybiphenyl *[92-88-6]* have been the subject of attention. In addition to the conventional synthesis via alkali fusion of the 4,4′-disulfonate (69,70), methods involving 4,4′-diiodobiphenyl *[3001-15-8]* (71) and the hydroperoxidation of 4,4′-diisopropylbiphenyl (72) are under development. An alternative commercial route to 4,4′-dihydroxybiphenyl, practiced by Dart Industries, involves oxidative coupling of 2,6-di*tert*-butylphenol *[128-39-2]* followed by dealkylation of the tetraalkylbiphenyl formed. Details of this process have been reviewed (73). 4,4′-Diisopropylbiphenyl can be oxidized to [1,1′-biphenyl]-4,4′dicarboxylic acid *[787-70-2]* (27) which is also an attractive polyester building block.

Semicommercial production of 3,3′,4,4′-biphenyltetracarboxylic dianhydride *[2420-87-3]* in the United States has been announced by Occidental Chemical Corp. (74). This polyimide resin intermediate is prepared by dehalogenative dimerization of 4-chlorophthalate salts (75) or by oxidative coupling of phthalate esters (76).

Nearly all of the terphenyls produced both in the United States and abroad are partially hydrogenated to afford a complex hydrocarbon mixture *[61788-32-7]* in which approximately 40% of the aromatic rings have been reduced. Producers may vary the degree of hydrogenation to some extent as well as the amount of quaterphenyls allowed to accompany the terphenyl feed cut. Economics favor maximum inclusion, but viscosity specifications usually enforce a limit of around 25%. Terphenyls can be hydrogenated over a variety of catalysts with Raney nickel preferred for the commercial process. Hydrogenated terphenyls are produced in the United States and United Kingdom by Monsanto. Other producers include Bayer (Germany), Nippon Steel (Japan), and Russia.

Hydrogenated terphenyls are widely used in industrial heat-transfer systems operating in the 0°C to 340°C range. An application receiving increased attention involves their use as a direct heating medium for the condensation of polyester oligomers to ultrahigh molecular weight polyesters (77). Reduced terphenyls, either alone or in mixtures, are employed as dye solvents by European carbonless copy paper producers. Consumption in this area has declined over the past decade. Hydrogenated terphenyls are also used in certain plasticizer applications, primarily PVC. Minor amounts are sold for various other uses (lubricant, hydraulic, nuclear reactor coolant, etc).

Worldwide production of hydrogenated terphenyls is estimated to be around 9 million kg yr with demand remaining fairly steady. Current U.S. prices are in the range of $5.50–6.05 kg.

Safety. Hydrogenated terphenyls are low in toxicity as the following data (78) indicate. Single exposure (acute) studies show:

oral LD_{50} (rat) = >10 g kg
dermal LD_{50} (rabbit) = >2.0 g kg
inhalation LC_{50} (rat 4 h) = >4.7 mg L
eye irritation (rabbit, 24 h) = 0.3 on a scale of 110
skin irritation (rabbit, 24 h) = 0.1 on a scale of 8.

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BISMUTH AND BISMUTH ALLOYS

The element bismuth *[7440-69-9]*, Bi, found in Group 15 (VA) of the Periodic Table, has at no. 83, at wt 208.98. Its valences are +5 and +3. Bismuth is a silvery metal having a high metallic luster and exhibits a slightly pink tinge on a cleanly broken surface. The metal itself is brittle in nature and easily broken.

Georgius Agricola, a German scientist of the sixteenth century, was the first to mention bismuth detailing the melting of bismuth from ore (1). It was in the sixteenth century that bismuth compounds were first discovered to have a soothing effect on stomach disorders. Bismuth compounds are still widely used in preparations to relieve this condition. Not until the 1800s was bismuth refined and proven to be an element. Until that time, bismuth was usually referred to as one of the other elements with which it is associated in ores such as antimony, silver, lead, and tin.

Occurrence

Bismuth is referred to as a minor metal. It is not generally mined for its own intrinsic value, rather it is mined primarily as a by-product of lead or copper ores. In China, however, bismuth can be found in tungsten ores. In Bolivia the metal has been mined for its own value, but this has not happened on a consistent basis over the years because fluctuations in the bismuth price have at times made it uneconomical to recover.

Bismuth occurs in the earth's crust in a concentration of approximately 0.1 ppm on the average. Higher concentrations of bismuth occur in oceanic manganese nodules in a range of 0.5 to 24 ppm (see OCEAN RAW MATERIALS). The next highest concentration of bismuth is found in silicic rock at 0.02 to 0.9 ppm (2).

Properties

The physical properties of bismuth, summarized in Table 1, are characterized by a low melting point, a high density, and expansion on solidification. Thermochemical and thermodynamic data are summarized in Table 2. The solid metal floats on the liquid metal as ice floating on water. Gallium and antimony are the only other metals that expand on solidification. Bismuth is the most diamagnetic of the metals, and it is a poor electrical conductor. The thermal conductivity of bismuth is lower than that of any other metal except mercury.

Table 1. Physical Properties of Bismuth

Property	Value
bp, °C	1.560
Bi–Bi bond length at 25°C, nm	0.309
crystal ionic radius, nm	
Bi^{+}	0.098
Bi^{3+}	0.096
Bi^{5+}	0.074
crystal structure	rhombohedral
density, kg/m^3	
20°C	9,800
271°C[a]	9,740
271°C[b]	10,070
600°C	9,660
electrical resistivity, Ω·cm	
0°C	106×10^{-6}
20°C	120×10^{-6}
expansion on freezing, % by vol	3.3
hardness, Mohs' scale	2.5
magnetic susceptibility	
solid	280×10^{-13}
liquid	10.5×10^{-13}
mp, °C	271.3
vapor pressure, kPa[c]	
400°C	1.013×10^{-4}
600°C	1.013×10^{-1}
880°C	1.013×10^{2}
1420°C	1.013×10^{5}
viscosity, mPa·s(=cP)	
285°C	1.610
304°C	1.662
365°C	1.460
451°C	1.280
600°C	0.998

[a] Solid.

[b] Liquid.

[c] To convert kPa to psi, divide by 6.895×10^{3}.

Table 2. Thermochemical and Thermodynamic Properties of Bismuth

Parameter	Value		
entropy at 298 K, $\Delta S°$, J (mol·K)[a]	56.9		
entropy of transition, ΔS, J (mol·K)[a]			
solid	20.2		
liquid	90.4		
heat capacity, ΔC_p, J (kg·K)[a]			
173.15°C	108		
25°C	122		
25–271°C	$4.49-5.40 \times 10^{-3}T$[b]		
271–1027°C[c]	235[d]		
heat of fusion, ΔH_{fus}, kJ/kg[a]	51.816		
heat of transition, ΔH, J/mol[a]			
solid	11.0		
liquid	172		
heat of vaporization, ΔH_{vap}, kJ/kg[a]	858.29		
thermal conductivity, W/(m·K)			
	Temperature		
	0°C	25°C	100°C
parallel to triagonal axis	5.54	5.30	4.81
perpendicular to triagonal axis	9.53	9.19	8.44
polycrystalline	8.22	7.92	7.22
thermal expansion coefficient 20–100°C	(13.4×10^{-6})/K		

[a] To convert from J to cal, divide by 4.184.

[b] Temperature in degrees kelvin.

[c] Liquid.

[d] Units are J/(mol·K). To convert from J to cal, divide by 4.184.

Production

Bismuth is mined primarily as a by-product of the processing of ores of other metals, mostly copper and lead. The countries that mine significant quantities of bismuth are Australia, Bolivia, Canada, China, Japan, Mexico, Peru, and the United States. Production is summarized in Table 3.

Table 3. Annual Bismuth Production, t[a]

	Year				
World production[b]	1986	1987	1988	1989	1990
mine	3658	3173	3220	3556	3200[c]
refinery	4077	4078	4098	4082	3710[c]

[a] Ref. 3.

[b] Excluding the United States.

[c] Estimated.

In Australia, bismuth is mined as a by-product of copper ores by Peko-Wallsend Ltd. and exported for refining. Bolivia is the only country in the world where concentrations of bismuth are high enough that it is mined for its own value. The Tasna mine in Bolivia is thus unique. This mine was shut down for most of the 1980s, however, because the free-market price for bismuth dropped to a low value in the late 1970s and remained low through the early 1980s.

Mined bismuth in China is a by-product of tungsten mining operations, but most of the bismuth produced in China comes from bismuth concentrates.

The principal portion of the bismuth in copper (qv) ores follows the copper into the matte. During the conversion of the matte to blister copper most of the bismuth fumes off. The fumes are caught in the baghouse or Cottrell system along with other elements such as lead (qv), arsenic, and antimony. These dusts are transferred to the lead-smelting operation. The portion of the bismuth remaining with the blister copper is separated during the electrolytic refining in the slimes. The procedure for handling the slimes results in the bismuth being collected in the lead bullion (4).

The bismuth that is found in the lead ore accompanies the lead through the smelting operation right up to the last refining steps. The removal of bismuth then requires special techniques, the most common being the Betterton-Kroll and the Betts processes (5).

Betterton-Kroll Process. Metallic calcium and magnesium are added to the lead bullion in a melt and form ternary compounds that melt higher than lead and are lower in density. By cooling the lead bath to a temperature close to the melting point of lead, the intermetallic compounds high in bismuth content solidify and float to the top where they are removed by skimming.

This bismuth–calcium–magnesium dross also contains lead that must be removed. The dross is heated in a kettle to free any entrapped lead that melts and forms a pool under the dross. This lead is cast and returned to the bismuth separation cycle. The dross is then melted and treated with chlorine and/or lead chloride to remove the calcium and magnesium. The resulting molten metal is an alloy of bismuth and lead, high in bismuth which is then treated to produce refined bismuth metal.

Betts Electrolytic Process. The Betts process starts with lead bullion, which may carry tin, silver, gold, bismuth, copper, antimony, arsenic, selenium, tellurium, and other impurities, but should contain at least 90% lead (6,7). If more than 0.01% tin is present, it is usually removed from the bullion first by means of a tin-drossing operation (see TIN AND TIN ALLOYS, DETINNING). The lead bullion is cast as plates or anodes, and numerous anodes are set in parallel in each electrolytic cell. Between the anodes, thin sheets of pure lead are hung from conductor bars to form the cathodes. Several cells are connected in series.

The electrolyte is a solution of lead fluosilicate *[25808-74-6]*, $PbSiF_6$, and fluosilicic acid *[16961-83-4]*, H_2SiF_6, containing a small amount of glue or other suitable agent. Direct current is passed through the cells to dissolve the lead from the anodes and deposit it on the cathodes. The impurities in the lead anodes are insoluble under the conditions of normal cell operation and remain on the face of the anodes as a porous slime blanket. The finished cathodes are withdrawn form the cells, washed, and melted to refined lead. The scrap anodes are withdrawn, and the slime is washed free of soluble matter, either while still on the anode or after it has been removed by cleaning. The cleaned anode scrap is returned to the anode-casting kettle for recasting.

The washed slime is dried and melted to produce slag and metal. The slag is usually purified by selective reduction and smelted to produce antimonial lead. The metal is treated in the molten state by selective oxidation for the removal of arsenic, antimony, and some of the lead. It is then transferred to a cupel furnace, where the oxidation is continued until only the silver–gold alloy (dorii) remains. The bismuth-rich cupel slags are crushed, mixed with a small amount of sulfur, and reduced with carbon to a copper matte and impure bismuth metal; the latter is transferred to the bismuth refining plant.

The gases from the several furnaces treating the slimes carry bismuth, silver, gold, and other values as particulates, which are recovered via Cottrell precipitators, baghouses, or scrubbers.

Recovery of Bismuth from Tin Concentrates. Bismuth is leached from roasted tin concentrates and other bismuth-bearing materials by means of hydrochloric acid. The acid leach liquor is clarified by settling or filtration, and the bismuth is precipitated as bismuth oxychloride *[7787-59-9]*, BiOCl, when the liquors are diluted using large volumes of water. The impure bismuth oxychloride is usually redissolved in hydrochloric acid and reprecipitated by diluting several times. It is then dried, mixed with soda ash and carbon, and reduced to metal. The wet bismuth oxychloride may also be reduced to metal by means of iron or zinc in the presence of hydrochloric acid. The metallic bismuth produced by the oxychloride method requires additional refining.

The Sperry process for making white lead in an electrolytic cell recovers bismuth as a by-product in the anode slimes.

The crystallization process for concentrating bismuth in lead by squeezing the eutectic (high in bismuth) liquid out of the solidified high lead portion at a temperature within the melting range of the alloy is seldom used.

Refining. The alloy of bismuth and lead from the separation procedures is treated with molten caustic soda to remove traces of such acidic elements as arsenic and tellurium (4). It is then subjected to the Parkes desilverization process to remove the silver and gold present. This process is also used to remove these elements from lead.

The desilverized alloy now contains bismuth as well as lead and zinc. To remove the lead and zinc, advantage is taken of the fact that zinc and lead chlorides are formed before bismuth chloride *[7787-60-2]*, $BiCl_3$, when the alloy is treated at 500°C with chlorine gas. Zinc chloride *[7646-85-7]*, $ZnCl_2$, forms first, and after its removal lead chloride *[7758-95-4]*, $PbCl_2$, forms preferentially. This process is continued until the desired level of lead removal has been reached. The bismuth is given a final oxidation with air and caustic soda; the refined product has a purity of 99.999%.

Fabrication. There are four basic forms of bismuth that are readily available commercially: ingot, needle, pellet, and powder. Bismuth ingots range from 4.5 to 13.6 kg each depending on the producer. Ingots are used mostly in metallurgical additives and in making fusible alloys. Bismuth needle is typically 0.16 cm (0.0625 in.) in diameter by nominally 2.54 cm in length. Needle is used primarily in the production of bismuth compounds for pharmaceutical and catalyst applications. Bismuth powder is produced in varying mesh sizes for the electronics industry.

Bismuth pellets range from 4.5 to 60 g in size and are used for metallurgical additives. Their convenient size and specific weights make them particularly useful as feedstock when a given quantity of bismuth must be added regularly to a melt.

Economic Aspects

The United States is highly dependent on bismuth imports because domestic usage greatly outruns domestic production. In 1990, the United States imported 1612 t of bismuth (3). The primary sources are Belgium, Mexico, and Peru. Substantial quantities of metal were also imported from Canada, China, Germany, and the United Kingdom. A small quantity of bismuth was imposed from Japan.

The supply of bismuth metal, is dependent on the supply of the associated metals with which it is mined. Since the 1970s bismuth prices have ranged from less than $4.40 kg to over $44 kg because of supply and demand. The price reached an all time high of over $44 kg in May of 1974 and fell to an all time low of under $3.30 kg in the summer of 1982. Bismuth finished off 1990 at $6.17–6.39 kg (8).

Uses

The three primary categories of uses of bismuth in industry, chemical, metallurgical additive, and fusible alloy, and the respective quantities, are given in Table 4. The chemical category can be broken down into pharmaceuticals, cosmetics, catalysts, industrial pigments, and electronics; the metallurgical additive category into steel, aluminum, and cast-iron additives. The fusible alloy category is divisible into more than a dozen subcategories dependent on specific application.

Table 4. Annual United States Consumption of Bismuth Metal, t[a]

	Year				
Use	1986	1987	1988	1989	1990
chemicals[b]	663	748	679	659	577
fusible alloys	290	334	332	272	249
metallurgical additives	350	494	493	396	424
other[c]	21	21	27	25	24
Total[d]	*1324*	*1597*	*1531*	*1352*	*1274*

[a] Ref. 3.

[b] Includes industrial and laboratory chemicals, cosmetics, and pharmaceuticals.

[c] Includes other alloys and experimental uses.

[d] Data may not add to totals shown because of independent rounding.

Until 1930, approximately 90% of bismuth usage was for pharmaceutical applications (9). From that point until the 1970s, research produced new applications that greatly expanded the uses of the metal. At that point the pharmaceutical use accounted for about 50% of the total bismuth consumption. By 1991, the fusible alloy category along with the other subdivisions each accounted for about 10% of the bismuth usage. Pharmaceutical usage was down to 20%.

As a metallurgical additive, bismuth is used in the manufacturing of free-machining steel and free-machining aluminum. Bismuth is added in pellet, granule, or shot form into the pouring stream during filling of the ingot mold. The amount of bismuth added can range from 0.003–0.10% depending on the type of steel. The bismuth addition enhances the action of lead in the steel by producing less frictional resistance at the cutting edge of the tool. This produces thinner and smaller chips, higher productivity, and better surface finish.

Bismuth Alloys

Because bismuth expands on solidification and because it alloys with certain other metals to give low melting point alloys, bismuth is particularly well suited for a number of uses. Alloys of bismuth can be made that expand, shrink, or remain dimensionally stable on solidification. All other metals except gallium and antimony contract on solidification. Bismuth alloys and uses are summarized in Table 5.

Table 5. Alloy Compositions and Uses

Melting point, °C	Composition, wt %						Uses[a]
	Bismuth	Lead	Tin	Cadmium	Indium	Antimony	
47	44.7	22.6	8.3	5.3	19.1	0.0	LB
58	49.0	18.0	12.0	10.0	21.0	0.0	LB
70	50.0	26.37	13.3	10.0	0.0	0.0	RS, W, LB
101	39.4	29.8	30.8	0.0	0.0	0.0	FSD
124	55.5	44.5	0.0	0.0	0.0	0.0	PC
138	58.0	0.0	42.0	0.0	0.0	0.0	W, SMF, FC
138 170	40.0	0.0	60.0	0.0	0.0	0.0	IC

[a] LB lens blocking; W work holding; RS radiation shielding; FSD fusible safety device; PC proof casting; SMF sheet metal forming; FC fusible cores; IC investment casting.

Uses of Alloys.

Anchoring. Bismuth alloys that expand on solidification are particularly useful for aligning and setting punches in a die plate. It is much easier to melt and pour an alloy around a punch than to machine the entire die plate and punch at the same time. This method also makes it easier to relocate parts or change dies. The low temperatures involved do not cause distortion.

Radiation Shielding. Like lead, bismuth absorbs radiation. Therefore, bismuth alloys are widely used in the medical industry during radiation therapy. The alloy is molded to the shape of various organs that are to be shielded. Then the molds are placed between the radiation source and the patient to protect the patient's vital organs from radiation exposure.

Electromagnetic and Radiofrequency Shielding. Because bismuth is highly diamagnetic, its alloys are quite useful in applications where electronic equipment must be protected from outside interference or where equipment can cause outside interference.

Tube Bending. The search for high strength, low weight structural materials produced the use of hollow tubes of many metals and alloys as structural components. These materials must often be bent and shaped to fit. Bending an empty tube causes distortion of the shape of the tube by flattening or wrinkling. These tubes can be filled with a low melting bismuth alloy that allows the tube to be bent as if it were solid, thus eliminating distortion. Then the alloy can be easily melted out of the tube and reused.

Fusible Safety Devices. Low melting bismuth alloys, especially those that are eutectic have found numerous uses in safety devices. These alloys can be cast into any shape necessary in order to be used in a plug or switch that must function at a given temperature.

Lens Blocking. Bismuth alloys have become particularly useful in the optical industry for securing lenses for grinding processes. The low melting point provides that the lenses may be secured without preheating. The alloys have high strength so that good control is maintained during the grinding process. These alloys then are easily removed by melting in hot water and then reused.

Fusible Cores. The use of low melting bismuth alloys has made it possible to produce items having complex internal cavities that cannot be produced using conventional core molds. These alloys are dimensionally stable so that when they are cast they result in a core piece having the most exact detail and surface finish required. These alloys are being used in the electroforming industry as well as the plastics industry where cost and weight reduction have become critical. Once molding or electroforming is complete the part is immersed in a heat bath that melts out the alloy for reuse.

Steel Quenching. Bismuth and bismuth–lead alloys are used in the processing of some steel products. The thermal conductivity of bismuth makes it ideal for use in quenching steel. The use of a bismuth–lead alloy in place of lead alone has the advantage of lowering the operating temperature of the bath as well as reducing adherence of alloy to the steel.

Proof Casting of Dies and Molds. Low melting alloys make the process of diemaking faster and easier. The low temperature alloys can be cast into a mold pattern at virtually any point in the manufacturing process without long delays in production and without the possibility of heat distortion. These alloys produce a casting that is exact in detail, requires no curing time, and is completely reusable.

Work Holding and Work Supporting. Low melting bismuth alloys have been used to solve two problems in machining operations. First, these alloys are used to hold parts that need machining but have no regular side that can be clamped. Second, bismuth alloys provide a method of support for parts such as turbine blades that are not stiff enough to stand alone for machining.

Sheet Metal Forming Dies. Engineers have found that low melting alloys, because they are tough and durable, are suitable for making castings that produce hundreds of pressings in sheet metal of normal materials from aluminum to titanium. Once a given short run of pressings is complete, the tooling can easily be melted and used for another tooling job.

Safety No industrial poisoning from bismuth has been reported (10). However, precautions should be taken against the careless handling of bismuth and its compounds; ingestion and inhalation of dusts and fumes should be avoided.

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BISMUTH COMPOUNDS

Bismuth is the fifth member of the nitrogen family of elements and, like its congeners, possesses five electrons in its outermost shell, $6s^2 6p^3$. In many compounds, the bismuth atom utilizes only the three $6p$ electrons in bond formation and retains the two $6s$ electrons as an inert pair. Compounds are also known where bismuth is bonded to four, five, or six other atoms. Many bismuth compounds do not have simple molecular structures and exist in the solid state as polymeric chains or sheets.

The +3 oxidation state is exhibited by bismuth in the vast majority of its compounds. A few inorganic and a variety of organic compounds, however, contain the element in the +5 state. Other rarer oxidation states reported for bismuth include +2, +1, and 3. Bismuth also forms polynuclear ionic species with oxidation states that are usually fractional and range from 1 to +1.

Technical information concerning bismuth and its compounds is distributed periodically by the Bismuth Institute, a nonprofit organization incorporated in La Paz, Bolivia, that has an information center in Brussels.

The United States consumed 1500 metric tons of bismuth in 1988 and exported 147 t (1). The average domestic dealer price was $12.74 kg. The world mine output, excluding the United States, was estimated to be 2770 t in 1988; the world refinery production was estimated as 3510 t. Of the bismuth consumed in the United States, 679 t was used for industrial and laboratory chemicals, cosmetics (qv), and pharmaceuticals (qv); 333 t for fusible alloys; 493 t for metallurgical additives; 12 t for other alloys; and 15 t for miscellaneous purposes.

Analysis

Many of the methods used for the determination of bismuth are not very selective; thus it is often necessary to separate it from interfering substances. A gravimetric method for the determination of bismuth in drugs, in the absence of lead, is described in considerable detail (2). A polarographic method for bismuth in drugs is also described in the same volume. The direct titration of bismuth, using the disodium salt of ethylenediaminetetraacetic acid (EDTA), has been found to be the best general method for determining macro and semimicro quantities of bismuth (3). The method is fast, convenient, and accurate. Few foreign ions in moderate amounts interfere. The titration is best carried out at a pH between 1.5 and 2.0. When the end point is detected by photometric methods, the titration of bismuth as dilute as 10^{-6} molar is feasible. Several photometric methods have been described for determining trace amounts of bismuth in ores or in nonferrous alloys using reagents such as dithizone, thiourea, potassium iodide, or dimercaptothiopyrone (4). Differential anodic stripping voltammetry has also been used for the determination of small amounts (5 µg L) of bismuth (5).

For the determination of trace amounts of bismuth, atomic absorption spectrometry is probably the most sensitive method. A procedure involving the generation of bismuthine by the use of sodium borohydride followed by flameless atomic absorption spectrometry has been described (6). The sensitivity of this method is given as 10 pg 0.0044 A, where A is an absorbance unit; the precision is 6.7% for 25 pg of bismuth. The low neutron cross section of bismuth virtually rules out any determination of bismuth based on neutron absorption or neutron activation.

Inorganic Compounds of Bismuth

Bismuthine. Bismuthine *[18288-22-7]*, BiH_3, is a colorless gas, unstable at room temperature, but isolatable as a colorless liquid at lower temperatures. Owing to its instability and difficulty of preparation, no more than a few hundred milligrams of the pure compound have been available for any single study. Vapor-pressure data from 116 to 43°C have been determined, and by extrapolation, a normal boiling point of +16.8°C has been indicated; ΔH_v, calculated from the same data, is 25.15 kJ mol (6.01 kcal mol) (7).

The existence of bismuthine was first demonstrated by using a radioactive tracer, ^{212}Bi (8). Acid treatment of a magnesium plate coated with ^{212}Bi resulted in the liberation of a volatile radioactive compound. In subsequent experiments, magnesium bismuthide *[12048-46-3]*, Mg_3Bi_2, was treated with acid; the yield, however, was only one part of bismuthine for every 20,000 parts of bismuth dissolved. Attempts to prepare bismuthine by reduction of bismuth trichloride with a borohydride have not been particularly successful. Experimental quantities are best prepared by disproportionation of either methylbismuthine *[66172-95-0]*, CH_5Bi, or dimethylbismuthine *[14381-45-4]*, C_2H_7Bi (7):

$$(CH_3)_{3-n}BiH_n \rightarrow n\ 3BiH_3 + (3-n)\ 3(CH_3)_3Bi$$

In the case of methylbismuthine, the disproportionation occurs upon keeping the compound at 45°C for several hours; 389.1 mg of methylbismuthine yields 241.1 mg of BiH_3.

At room temperature bismuthine rapidly decomposes into its elements. The rate of decomposition increases markedly at higher temperatures (8). Bismuthine decomposes when bubbled through silver nitrate or alkali solutions but is unaffected by light, hydrogen sulfide, or 4 N sulfuric acid solution. There is no evidence for the formation of BiH_4^+, though the phenyl derivative, $(C_6H_5)_4Bi^+$, is known. The existence of BiH_4^+ would not be anticipated on the basis of the trend found with other Group 15 (V) "onium" ions.

Bismuthides. Many intermetallic compounds of bismuth with alkali metals and alkaline earth metals have the expected formulas M_3Bi and M_3Bi_2, respectively. These compounds are not saltlike but have high coordination numbers, interatomic distances similar to those found in metals, and metallic electrical conductivities. They dissolve to some extent in molten salts (eg, NaCl–NaI) to form solutions that have been interpreted from cryoscopic data as containing some Bi_3^{3-}. Both the alkali and alkaline earth metals form another series of alloylike bismuth compounds that become superconducting at low temperatures (Table 1). The MBi_2 compounds are particularly noteworthy as having extremely short bond distances between the alkali metal atoms.

Table 1. Alloylike Superconducting Bismuth Compounds

Compound	CAS Registry Number	Formula	Temp,[a] K
lithium bismuthide	*[12048-27-0]*	LiBi	2.47
sodium bismuthide	*[12258-63-8]*	NaBi	2.22
potassium dibismuthide	*[12431-17-3]*	KBi_2	3.58
rubidium dibismuthide	*[55127-10-1]*	$RbBi_2$	4.25
cesium dibismuthide	*[12233-24-8]*	$CsBi_2$	4.75
calcium tribismuthide	*[66271-89-4]*	$CaBi_3$	1.7
strontium tribismuthide	*[12589-81-0]*	$SrBi_3$	5.62

barium tribismuthide	*[12047-02-8]*	$BaBi_3$	5.69

[a] Temperature below which the compound is superconducting.

Bismuth Halides. The bismuth trihalides are the best known. Bismuth does form a single pentahalide, BiF_5, and subhalides that approximate the composition BiX, the best characterized of these being $BiCl_{1.17}$. Vapors above solutions of a bismuth trihalide in molten bismuth contain the species BiX and or $(BiX)_n$, where X Cl, Br, or I (9). At temperatures below 323°C, a black, diamagnetic, orthorhombic solid of the overall composition $BiCl_{1.17}$ may be isolated from solutions of bismuth trichloride in molten bismuth (10).

Direct halogenation of metallic bismuth yields bismuth pentafluoride in the case of fluorine, the corresponding bismuth trihalides for the other halogens. Reaction of bismuth trioxide with aqueous HF, HCl, or HBr yields the corresponding bismuth trihalide. Physical and thermochemical properties of the more important bismuth halides appear in Table 2.

Table 2. Physical Properties of Bismuth Compounds

Bismuth compound	CAS Registry Number	Formula	MP, °C	Bp, °C	$\Delta H^\circ_{f,298}$, kJ/mol[a]	S°_{298}, J/mol·K[a]	$\Delta H^\circ_{f,fusion}$, kJ/mol[a]	$\Delta S^\circ_{f,fusion}$, J/mol·K[a]	$\Delta H^\circ_{sub,298}$, kJ/mol[a]	$\Delta S^\circ_{subl,298}$, J/mol·K[a]	Bi–X bond energy, kJ/mol[a]	References
bismuth trifluoride	*[7787-61-3]*	BiF_3	649[b]	900 ± 10	900 ± 13	123 ± 4	21.6 ± 0.6	23.4 ± 0.8	201 ± 3	195 ± 3	381	12
bismuth pentafluoride	*[7787-62-4]*	BiF_5	151	230								
bismuth trichloride	*[7787-60-2]*	$BiCl_3$	233.5	44.7	379	174 ± 6	23.9		114 ± 1	183 ± 2	279	13,14
bismuth monochloride	*[14899-70-8]*	BiCl			131	94.5					300 ± 4	13,15
bismuth oxychloride	*[7787-59-9]*	BiOCl			367	120						13
bismuth tribromide	*[7787-58-8]*	$BiBr_3$	219	441	276 ± 2	190 ± 1	21.8		115 ± 1	182 ± 1	233.0 ± 1.4	16
bismuth triiodide	*[7787-64-6]*	BiI_3	408.6	542[c]	151 ± 4	224.8 ± 0.8	39.1 ± 0.3	57.3 ± 0.4	134.3 ± 0.5	183.4 ± 0.8	181 ± 5	17,18
bismuth trioxide	*[1304-76-3]*	Bi_2O_3[d]	824		574	151.5						13
bismuth trisulfide	*[1345-07-9]*	Bi_2S_3	850		143	200						13
bismuth tritelluride	*[1304-82-1]*	Bi_2Te_3			77.4	260.9						13

[a] To convert J to cal, divide by 4.184.

[b] The mp frequently cited is 120°C higher than this and is, apparently, for material contaminated with oxyfluoride.

[c] The normal bp has been extrapolated from vapor-pressure data.

[d] Monoclinic.

Bismuth Trifluoride. Bismuth(III) fluoride is a white to grey-white powder, density 8.3 g/mL, that is essentially isomorphous with orthorhombic YF_3, requiring nine-coordination about the bismuth (11). It has been suggested that BiF_3 is best considered an eight-coordinate structure with the deviation from the YF_3 structure resulting from stereochemical activity of the bismuth lone-pair electrons. In accord with its structure, the compound is the most ionic of the bismuth halides. It is almost insoluble in water ($5.03 \pm 0.05 \times 10^{-3}$ *M* at pH 1.15) and dissolves only to the extent of 0.010 g per 100 g of anhydrous HF at 12.4°C.

Bismuth trifluoride is usually prepared by dissolving either Bi_2O_3 or BiOF in hydrofluoric acid to yield the addition compound bismuth trifluoride trihydrofluoride *[66184-11-0]*, $BiF_3 \cdot 3HF$ or $H_3(BiF_6)$. Careful evaporation of the solution permits isolation of a grey solid, which upon heating loses HF to yield BiF_3. It may be purified by sublimation in a stream of HF at 500°C. Bismuth trifluoride may also be prepared by direct fluorination of bismuth by: (*1*) reaction of Bi_2O_3 with sulfur tetrafluoride, SF_4; (*2*) treatment of metallic bismuth with HF at 350°C; and (*3*) reduction of BiF_5 in a dilute stream of hydrogen.

Bismuth trifluoride is not readily hydrolyzed even by boiling water. However, addition of HF causes the formation of $BiF_3 \cdot 3HF$, which is readily hydrolyzed to bismuth oxyfluoride *[13520-72-4]*, BiOF. Heating BiF_3 at 200–300°C in air results in the formation of some oxide or oxyfluoride. Between 600 and 800°C fluorine is gradually replaced by oxygen yielding phases such as $BiO_{0.1}F_{2.8}$, BiOF, and, on prolonged heating (60 h at 670°C), Bi_2O_3. The so-called cubic phase of BiF_3 probably contains some oxygen.

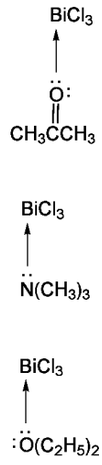
Complexes of BiF_3 are almost unknown, but crystallization from a hot solution of ammonium fluoride that has been saturated with freshly precipitated bismuth trioxide yields crystals of ammonium tetrafluorobismuthate(III) *[13600-76-5]*, NH_4BiF_4. This complex is readily decomposed by water.

Bismuth Trichloride. Bismuth(III) chloride is a colorless, crystalline, deliquescent solid made up of pyramidal molecules (19). The nearest intermolecular Bi–Cl distances are 0.3216 nm and 0.3450 nm. The density of the solid is 4.75 g/mL and that of the liquid at 254°C is 3.851 g/mL. The vapor density corresponds to that of the monomeric species. The compound is monomeric in dilute ether solutions, but association occurs at concentrations greater than 0.1 *M*. The electrical conductivity of molten $BiCl_3$ is of the same order of magnitude as that found for ionic substances.

Bismuth trichloride is usually prepared by chlorination of the molten metal or by dissolving bismuth metal in aqua regia; evaporation of the solution yields the bismuth trichloride dihydrate *[66172-88-1]*, $BiCl_3 \cdot 2H_2O$, and upon distillation, it decomposes to give anhydrous bismuth trichloride. The commercial product frequently is not anhydrous.

Bismuth trichloride shows considerable tendency to form addition compounds. Reaction with ammonia yields the colorless, easily volatilized bismuth trichloride triammine *[66172-89-2]*, $BiCl_3 \cdot 3NH_3$, as well as the red, thermally unstable bismuth trichloride hemiammine *[66172-90-5]*, $2BiCl_3 \cdot NH_3$. Compounds of formula $BiCl_3 \cdot NO$, $BiCl_3 \cdot 2NO_2$, and $BiCl_3 \cdot NOCl$ may be isolated; these are stable in dry air but are decomposed by moisture. Bismuth

trichloride is soluble in organic solvents; solution is presumably accompanied by the formation of complexes of the type:



A number of complex bismuth halides are well-known, eg, disodium bismuth pentachloride *[66184-10-9]*, Na_2BiCl_5; sodium dibismuth heptachloride *[66184-09-6]*, $NaBi_2Cl_7$; and trisodium bismuth hexachloride *[66114-82-7]*, Na_3BiCl . The acid, hydrogen dibismuth heptachloride trihydrate *[66124-39-9]*, $HBi_2Cl_7 \cdot 3H_2O$, is a crystalline substance, stable at room temperature, that may be isolated by cooling a solution of $BiCl_3$ in concentrated hydrochloric acid to 0°C.

Bismuth Tribromide. Bismuth(III) bromide is a hygroscopic, golden-yellow, crystalline solid made up of pyramidal molecules. X-ray analysis has shown that the three bromines are 0.263 ± 0.002 nm from the bismuth and the Br–Bi–Br angles are 100 ± 4°. More recent nqr experiments indicate that the bromines are not equivalent (20). The solid has a density of 5.72 g mL and that of the liquid is 4.572 g mL at 271.5°C.

Bismuth tribromide may be prepared by dissolving Bi_2O_3 in excess concentrated hydrobromic acid. The slurry formed is allowed to dry in air, then gently heated in a stream of nitrogen to remove water, and finally distilled in a stream of dry nitrogen. Bismuth tribromide is soluble in aqueous solutions of KCl, HCl, KBr, and KI but is decomposed by water to form bismuth oxybromide *[7787-57-7]*, BiOBr. It is soluble in acetone and ether, and practically insoluble in alcohol. It forms complexes with NH_3 and dissolves in hydrobromic acid from which dihydrogen bismuth pentabromide tetrahydrate *[66214-38-8]*, $H_2BiBr_5 \cdot 4H_2O$, may be crystallized at 10°C.

Bismuth Triiodide. Bismuth(III) iodide is a greenish black crystalline powder. The iodines are in a hexagonal close-packed array with each bismuth having six nearest-neighbor iodines at 0.32 nm (21). This suggests that the lone pair on bismuth is stereochemically inactive and that the compound is largely ionic in character.

Bismuth triiodide may be prepared by heating stoichiometric quantities of the elements in a sealed tube. It undergoes considerable decomposition at 500°C and is almost completely decomposed at 700°C. However, it may be sublimed without decomposition at 3.3 kPa (25 mm Hg). Bismuth triiodide is essentially insoluble in cold water and is decomposed by hot water. It is soluble in liquid ammonia forming a red triammine complex, absolute alcohol (3.5 g 100 g), benzene, toluene, and xylene. It dissolves in hydroiodic acid solutions from which hydrogen tetraiodobismuthate(III) *[66214-37-7]*, $HBiI_4 \cdot 4H_2O$, may be crystallized, and it dissolves in potassium iodide solutions to yield the red compound, potassium tetraiodobismuthate(III) *[39775-75-2]*, $KBiI_4$. Compounds of the type tripotassium bismuth hexaiodide *[66214-36-6]*, K_3BiI , are also known.

Bismuth Pentafluoride. Bismuth(V) fluoride consists of long white needles that have been shown to have the same structure as the body-centered, tetragonal α-polymorph of uranium hexafluoride. The density of the solid is 5.4 g mL at 25°C. The solid consists of infinite chains of trans-bridged BiF polyhedra; dimers and trimers are present in the vapor phase (22). Bismuth pentafluoride may be prepared by the fluorination of BiF_3 or metallic bismuth at 600°C. For purification, it may be separated from BiF_3 by repeated sublimation at 120°C. At higher temperatures it decomposes to yield BiF_3 and fluorine.

Bismuth pentafluoride is an active fluorinating agent. It reacts explosively with water to form ozone, oxygen difluoride, and a voluminous chocolate-brown precipitate, possibly a hydrated bismuth(V) oxyfluoride. A similar brown precipitate is observed when the white solid compound bismuth oxytrifluoride *[66172-91-6]*, $BiOF_3$, is hydrolyzed. Upon standing, the chocolate-brown precipitate slowly undergoes reduction to yield a white bismuth(III) compound. At room temperature BiF_5 reacts vigorously with iodine or sulfur; above 50°C it converts paraffin oil to fluorocarbons; at 150°C it fluorinates uranium tetrafluoride to uranium pentafluoride; and at 180°C it converts Br_2 to bromine trifluoride, BrF_3, and bromine pentafluoride, BrF_5, and chlorine to chlorine fluoride, ClF. It apparently does not react with dry oxygen.

Treatment of BiF_5 with BrF_3 results in the formation of fluorobromonium hexafluorobismuthate(V) *[36608-81-8]*, $[BrF_2][BiF$], which may be isolated as white hygroscopic crystals upon removal of excess BrF_3 under vacuum. This compound is relatively stable but at reduced pressures undergoes decomposition to BrF_3 and BiF_5. Adducts are formed between BiF_5 and the fluorides of lithium, sodium, potassium, or silver by heating equimolar quantities of the respective compounds to 85–150°C. The resulting hexafluorobismuthate(V) compounds are more stable to reduction than BiF_5. The x-ray diffraction pattern of potassium hexafluorobismuthate(V) *[26914-71-6]*, KBiF , is similar to that of potassium hexafluoroantimonate(V) *[16893-92-8]*, KSbF . Silver hexafluorobismuthate(V) *[66184-08-5]*, AgBiF , may also be formed by warming elemental silver and $[BrF_2][BiF$] dissolved in BrF_3. This compound is hygroscopic, soluble in HF, and reacts with water to form a chocolate-brown precipitate and probably some ozone.

Bismuth Oxide Halides. Hydrolysis of a bismuth trihalide yields the corresponding bismuth(III) oxide halide (oxyhalide). Bismuth oxyfluoride *[13520-72-4]*, BiOF, and bismuth oxyiodide *[7787-63-5]*, BiOI, may also be formed by heating the corresponding bismuth trihalide in air. When either bismuth oxychloride or bismuth oxybromide *[7787-57-7]*, BiOBr, is heated above 700°C, complex bismuth oxyhalides of composition $Bi_{24}O_{31}X_{10}$ are formed. Bismuth oxychloride *[7787-59-9]*, BiOCl, is a white, lustrous, crystalline powder (density, 7.72 g mL) that is practically insoluble in water, alcohol, acids, and bases. Hot concentrated alkali solutions convert it to bismuth trioxide. It is used in fingernail polishes, lipsticks, and face powders to give a nacreous effect. A study (23) in which rats were fed 1, 2, or 5% BiOCl for two years showed no carcinogenic or toxic effects. Bismuth oxybromide, a white, amorphous powder, and bismuth oxyiodide, a brick-red, amorphous powder having a density of 7.92 g mL, are essentially insoluble in water, alcohol, acids, and bases and have been used in the manufacture of dry-cell cathodes.

Bismuth Oxides and Bismuthates. The only oxide of bismuth that has been definitely isolated in a pure state is bismuth trioxide. An acidic oxide that approximates the composition Bi_2O_5 certainly exists. However, there is considerable question as to the exact nature of this material and the species involved. A number of other oxides have been reported, eg, bismuth oxide (1:1) *[1332-64-5]*, bismuth oxide (1:2), bismuth oxide (2:4) *[12048-50-9]*, bismuth oxide (3:5), and bismuth oxide (4:9), but the evidence for their existence as chemical entities is meager at best.

Bismuth Trioxide. Bismuth(III) oxide *[1304-76-3]* has a complicated polymorphism. At times some of the reported phases deviate from Bi_2O_3 by having too little or too much oxygen; at least in one instance, because of the ready contamination of Bi_2O_3 melts with silicon, the reported phase probably has the composition of bismuth oxide silicate *[66256-73-3]*, $Si_2Bi_{24}O_{40}$. The common oxide, α-Bi_2O_3, is a pale-yellow, monoclinic solid,

density 9.32 ± 0.02 g mL, which is stable up to 710°C. Half of the bismuth atoms are five-coordinate, and half are six-coordinate. The lone-pair electrons on bismuth presumably occupy the sixth position for the five-coordinate bismuth and are responsible for the distortion of the oxygen about the six-coordinate bismuth (24).

Bismuth trioxide may be prepared by the following methods: (*1*) the oxidation of bismuth metal by oxygen at temperatures between 750 and 800°C; (*2*) the thermal decomposition of compounds such as the basic carbonate, the carbonate, or the nitrate (700–800°C); (*3*) precipitation of hydrated bismuth trioxide upon addition of an alkali metal hydroxide to a solution of a bismuth salt and removal of the water by ignition. The gelatinous precipitate initially formed becomes crystalline on standing; it has been represented by the formula $Bi(OH)_3$ and called bismuth hydroxide *[10361-43-0]*. However, no definite compound has been isolated.

Bismuth trioxide is practically insoluble in water; it is definitely a basic oxide and hence dissolves in acids to form salts. Acidic properties are just barely detectable, eg, its solubility slightly increases with increasing base concentration, presumably because of the formation of bismuthate(III) ions, such as $Bi(OH)_4^-$ and related species.

Bismuth trioxide forms numerous, complex, mixed oxides of varying composition when fused with CaO, SrO, BaO, and PbO. If high purity bismuth, lead, and copper oxides and strontium and calcium carbonates are mixed together with metal ratios Bi:Pb:Sn:Ca:Cu 1.9 : 0.4 : 2 : 2 : 3 or 1.95:0.6:2:2:3 and calcined at 800–835°C, the resulting materials have the nominal composition $Bi_{1.9}Pb_{0.4}Sr_2Ca_2Cu_3O_x$ and $Bi_{1.95}Pb_{0.6}Sr_2Ca_2Cu_3O_x$ and become superconducting at about 110 K (25).

Higher Oxides of Bismuth and Related Compounds. Oxidation of either a fused mixture of sodium oxide and bismuth trioxide or a suspension of bismuth trioxide in 40–50% sodium hydroxide solution yields a product in which much of the bismuth is apparently in the +5 oxidation state. Air or oxygen are suitable oxidizing agents for the molten mixture; sodium hypochlorite, chlorine, bromine, or sodium persulfate may be used for the aqueous suspension. The reactions are favored by excess alkali, and though more than 90% of the bismuth is oxidized to the pentacovalent state, the product is contaminated with considerable excess alkali. Extraction with methanol at 0°C removes the excess alkali and yields pure sodium metabismuthate(V) *[12232-99-4]*, $NaBiO_3$. Addition of nitric or perchloric acid produces a material ranging in composition from Bi_2O_4 to Bi_2O_5, which slowly loses oxygen. This material and sodium metabismuthate(V) are very good oxidizing agents. The sodium bismuthate of commerce varies in color from yellow to brown to black. It has about two molecules of water per bismuth atom and is insoluble in water. It is capable of oxidizing manganese(II) compounds in nitric acid solution to permanganate, a reaction commonly used as a qualitative test for manganese. $NaBiO_3$ oxidizes Fe^{3+} in basic medium to FeO_4^{2-}.

Sulfides and Related Compounds.

Bismuth Trisulfide. Bismuth(III) sulfide *[1345-07-9]*, bismuth sesquisulfide, Bi_2S_3, is a dark-brown to grayish black crystalline solid, mp 850°C and density of 6.78 g mL. It occurs naturally as the mineral bismuth glance and is isostructural with stibnite, Sb_2S_3. It may be prepared by heating sulfur and bismuth or by the addition of a soluble sulfide to an aqueous solution of bismuth(III). It is almost insoluble in water or alkaline solutions but dissolves in concentrated nitric acid or hot concentrated hydrochloric acid. Concentrated alkali metal sulfide solutions or melts dissolve Bi_2S_3 to yield crystalline compounds such as potassium thiobismuthate(III) *[12506-13-7]*, $KBiS_2$. These compounds are rapidly oxidized in air; similar compounds of silver, copper, and lead occur naturally. Fusion of Bi_2S_3 with a bismuth halide yields air-stable compounds, bismuth chlorosulfide *[19264-19-8]*, BiClS, bismuth bromosulfide *[14794-86-6]*, BiBrS, and bismuth iodosulfide *[15060-32-9]*, BiIS. Other mixed halide sulfide compounds have been reported: bismuth bromide sulfide (19:3:27) *[51185-13-8]*, $Bi_{19}S_{27}Br_3$, has been shown to consist of $(Bi_4S_{27})_\infty$ chains in which bismuth atoms in neighboring chains are linked by bromines (26). Bismuth disulfide *[12323-18-1]*, BiS_2, can be prepared at 5000 MPa at 1250°C. The compound is a soft, gray, needlelike, crystalline solid.

Bismuth trisulfide has been used as a high temperature lubricant and has been of interest for its photo- and thermoelectric properties.

Related Compounds. Bismuth triselenide *[12068-69-8]*, Bi_2Se_3, and bismuth tritelluride *[1304-82-1]*, Bi_2Te_3, are known, and in addition to the stoichiometric compounds, preparations can be made containing excess Bi, Se, or Te. Compounds are also known in which some of the Te in Bi_2Te_3 is replaced by S or Se and some of the Se in Bi_2Se_3 by S, eg, dibismuth ditellurium selenide *[12010-72-9]*, Bi_2Te_2Se and dibismuth ditellurium sulfide *[1304-78-5]*, Bi_2Te_2S. All of these materials are of interest for their semiconducting properties (see SEMICONDUCTORS).

Bismuth Salts. Bismuth trioxide dissolves in concentrated solutions of strong oxyacids to yield bismuth salts. In more dilute solutions of strong acids or in solutions of weak acids, the oxide reacts to form bismuthyl or basic salts. The normal salts are very susceptible to hydrolysis.

Bismuth Triperchlorate Pentahydrate. Bismuth(III) perchlorate pentahydrate *[66172-92-7]*, $Bi(ClO_4)_3 \cdot 5H_2O$, is prepared by dissolving Bi_2O_3 in 70% $HClO_4$. Anhydrous bismuth triperchlorate *[14059-45-1]*, $Bi(ClO_4)_3$, may be prepared by heating bismuthyl perchlorate monohydrate *[66172-93-8]*, $BiOClO_4 \cdot H_2O$, between 80 and 100°C. Attempts to dissolve bismuth metal in concentrated perchloric acid have resulted in explosions. Treatment of bismuth or Bi_2O_3 with dilute solutions of perchloric acid yields hydrates of bismuthyl perchlorate.

Bismuth Trinitrate Pentahydrate. Bismuth(III) nitrate pentahydrate *[10035-06-0]*, $Bi(NO_3)_3 \cdot 5H_2O$, is obtained by dissolving bismuth metal, Bi_2O_3, or $(BiO)_2CO_3$ in nitric acid. Attempts to remove the water of hydration yield monoclinic crystals of bismuthyl nitrate hemihydrate *[10361-64-3]*, $BiONO_3 \cdot 1/2H_2O$ (27). Addition of bismuth trinitrate pentahydrate to alkali yields a product termed bismuth subnitrate which is widely used in pharmaceuticals. This material approximates the composition $6Bi_2O_3 \cdot 5N_2O_5 \cdot 9H_2O$.

Bismuth Trisulfate. Bismuth(III) sulfate *[7787-68-0]*, $Bi_2(SO_4)_3$, is a colorless, very hygroscopic compound that decomposes above 405°C to yield bismuthyl salts and Bi_2O_3. The compound hydrolyzes slowly in cold water and rapidly in hot water to the yellow bismuthyl sulfate *[12010-64-9]*, $(BiO)_2SO_4$. The normal sulfate is isomorphous with the sulfates of yttrium, lanthanum, and praseodymium.

Numerous other bismuth and bismuthyl salts are known, eg, bismuth triacetate *[22306-37-2]*, $Bi(C_2H_3O_2)_3$; bismuth phosphate *[10049-01-1]*, $BiPO_4$; bismuth trithiocyanate *[43384-63-0]*, $Bi(CNS)_3$; bismuthyl nitrite hemihydrate *[66172-94-9]*, $BiO(NO_2) \cdot 1/2H_2O$; bismuthyl carbonate hemihydrate *[5798-45-8]*, $(BiO)_2CO_3 \cdot 1/2H_2O$; etc. Bismuth is present in the anion in the oxalato complex sodium dioxalatobismuthate(III) *[19033-91-1]*, $NaBi(C_2O_4)_2$, the nitrito complex $Na_3Bi(NO_2)_6$, trisodium hexanitrobismuthate(III) *[18515-86-1]*, and the yellow, water-soluble thiosulfato complex trisodium trithiosulfatobismuthate(III) *[66256-75-5]*, $Na_3Bi(S_2O_3)_3$.

Organobismuth Compounds

In a manner similar to phosphorus, arsenic, and antimony, the bismuth atom can be either tri- or pentacovalent. However, organobismuth compounds are less stable thermally than the corresponding phosphorus, arsenic, or antimony compounds, and there are fewer types of organobismuth compounds. For example, with R_4MX, R_3MX_2, R_2MX_3, and RMX_4, where M is a Group 15 (VA) element and X is a halogen, only the first two types have been prepared where M = Bi, but all four types are known where M = P, As, or Sb.

The chemistry of organobismuth compounds has been described in several publications (28–31). The use of organobismuth compounds, as well as organoantimony ones, in organic synthesis has been exhaustively reviewed (32).

Primary and Secondary Bismuthines. Only one primary and one secondary bismuthine are known, namely methylbismuthine, CH_3BiH_2, and dimethylbismuthine, $(CH_3)_2BiH$ (7). They are prepared by the lithium aluminum hydride reduction of methyldichlorobismuthine *[105309-90-8]*, CH_3BiCl_2, and dimethylchlorobismuthine, respectively, in a nitrogen atmosphere at −150°C. On being warmed to −45°C, methylbismuthine disproportionates to trimethylbismuthine *[593-91-9]*, $(CH_3)_3Bi$, and bismuthine. Dimethylbismuthine undergoes a similar disproportionation at −15°C. Both methyl- and dimethylbismuthine are stable, colorless liquids at −60°C, but at room temperature they decompose to trimethylbismuthine, bismuth,

and hydrogen. An attempt to prepare phenylbismuthine and diphenylbismuthine *[14381-43-2]*, $C_{12}H_{11}Bi$, by reduction of phenyldibromobismuthine *[39110-02-6]*, $C_6H_5BiBr_2$, and diphenylbromobismuthine *[39248-62-9]*, $C_{12}H_{10}BiBr$, respectively, with lithium aluminum hydride or sodium borohydride at low temperatures yielded only black polymeric substances of empirical formula C_6H_5Bi (33). It has been claimed (34) that dimethylbismuthine and diphenylbismuthine can be used as cocatalysts for the polymerization of ethylene (qv), propylene (qv), and 1,3-butadiene. The source of these bismuthines, however, was not mentioned.

Tertiary Bismuthines. A large number of trialkyl- and triarylbismuthines are known (29). They are usually prepared by the interaction of a reactive organometallic compound and a bismuth trihalide, a halobismuthine, or a dihalobismuthine. The Grignard reagent (see GRIGNARD REAGENTS) is the type of organometallic compound most widely employed in these syntheses (35–37). Organolithium (38–40), organoaluminum (41), organocadmium (42), organomercury (43), organosodium (44), organozinc (45,46), and organosilver (47) compounds have also been used. Triphenylbismuthine *[603-33-8]*, $C_{18}H_{15}Bi$, has been obtained in a 50% yield by the addition of phenyltrifluorosilane and ammonium fluoride to a solution of bismuth hydroxide in hydrofluoric acid (48). The interaction of organomercury compounds and metallic bismuth has also been employed for the preparation of tertiary bismuthines (49).

A number of tertiary bismuthines have been prepared by the interaction of a sodium diaryl- or dialkylbismuthide and an alkyl or aryl halide (50):

$$R_2BiNa + R^*X \rightarrow R_2R^*Bi + NaX$$

This method is of particular value for the preparation of unsymmetrical tertiary bismuthines.

Triarylbismuthines have been synthesized by means of the Nesmeyanov reaction that employs an arenediazonium salt such as the tetrafluoroborate, a bismuth trihalide, and a reducing agent (51). The decomposition of iodonium salts in the presence of bismuth trichloride and metallic bismuth also leads to the formation of triarylbismuthines, Ar_3Bi (52):

$$3\ ArAr'ICl + 2\ Bi \xrightarrow{BiCl_3} Ar_3Bi + BiCl_3 + 3\ Ar'I$$

Experiments with unsymmetrical iodonium salts indicate that the bismuth atom is preferentially arylated by the more electron-attracting aryl group.

There have been several reports of the formation of tertiary bismuthines by the action of free radicals on metallic bismuth. One method of generating the radicals involves cleavage of ethane or hexafluoroethane in a radiofrequency glow discharge apparatus; the radicals thus formed are allowed to oxidize the metal at −196°C (53). Trimethylbismuthine and tris(trifluoromethyl)bismuthine *[5863-80-9]*, C_3BiF_9, have been obtained by this procedure.

Other methods of preparing tertiary bismuthines have been used only to a limited extent. These methods include the electrolysis of organometallic compounds at a sacrificial bismuth anode (54), the reaction between a sodium–bismuth or potassium–bismuth alloy and an alkyl or aryl halide (55), the thermal elimination of sulfur dioxide from tris(arenesulfinato)bismuthines (56), and the interaction of ketene and a tris(dialkylamino)bismuthine (57).

Trialkylbismuthines are colorless or pale yellow liquids or solids, and most of them are spontaneously flammable in air. Except for trimethylbismuthine, these compounds cannot be distilled at ordinary pressures without decomposition (58). In general, trialkylbismuthines are not affected by water or aqueous bases but are readily hydrolyzed by many inorganic and organic acids. Hydrogen sulfide, mercaptans, and selenols appear to be particularly effective in cleaving the carbon–bismuth bond (59,60). Trialkylbismuthines generally react with chlorine and bromine at low temperatures to form dialkylhalobismuthines (45,46):

$$R_3Bi + X_2 \rightarrow R_2BiX + RX$$

The reaction of tris(trifluoromethyl)bismuthine with chlorine, bromine, or iodine, however, has been found to yield the corresponding bismuth trihalide and trifluoromethyl halide (61):

$$(CF_3)_3Bi + 3\ X_2 \rightarrow BiX_3 + 3\ CF_3X$$

Triarylbismuthines are solids, which usually have sharp melting points. Most of these compounds are unaffected by oxygen or water at ordinary temperature and are, in general, much less reactive than their trialkyl counterparts. Triphenylbismuthine can be readily distilled, bp 242°C at 1.9 kPa without decomposition, and it has been obtained so pure that it has been used in measurements of the atomic weight of bismuth (62). Most triarylbismuthines readily undergo oxidative addition with bromine or chlorine to yield the corresponding triarylbismuth dihalides:

$$Ar_3Bi + X_2 \rightarrow Ar_3BiX_2$$

Triphenylbismuth difluoride *[2023-48-5]*, $C_{18}H_{15}BiF_2$, has been obtained in a similar manner (63).

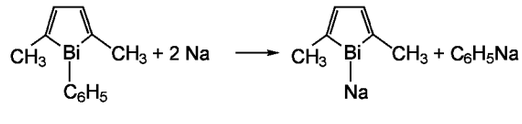
All three carbon–bismuth bonds of tribenzylbismuthine *[99715-52-3]*, $C_{21}H_{21}Bi$, (64) and triphenylbismuthine (65) can be cleaved by alkali metals. Under some conditions, however, tertiary bismuthines react with sodium or potassium to yield secondary bismuthides. Thus a number of sodium dialkylbismuthides have been obtained by the interaction of a trialkylbismuthine and sodium in liquid ammonia (66–69):

$$R_3Bi + 2\ Na \rightarrow R_2BiNa + RNa$$

where R = CH_3, C_2H_5, *n*-C_3H_7, iso-C_3H_7, or *n*-C_4H_9. Triphenylbismuthine reacts with potassium in tetrahydrofuran (THF) in a similar manner (70):

$$(C_6H_5)_3Bi + 2\ K \rightarrow (C_6H_5)_2BiK + C_6H_5K$$

Treatment of 1-phenyl-2,5-dimethylbismole *[88635-81-8]*, $C_{12}H_{13}Bi$, with sodium in liquid ammonia results in cleavage of the phenyl–bismuth bond and formation of 1-sodio-2,5-dimethylbismole *[88644-52-4]*, C_8H_8BiNa, (71):



The secondary bismuthides discussed herein are useful for preparing several types of organobismuth compounds, eg, tertiary bismuthines and dibismuthines.

Although trialkyl- and triarylbismuthines are much weaker donors than the corresponding phosphorus, arsenic, and antimony compounds, they have nevertheless been employed to a considerable extent as ligands in transition metal complexes. The metals coordinated to the bismuth in these complexes include chromium (72–77), cobalt (78,79), iridium (80), iron (77,81,82), manganese (83,84), molybdenum (72,75–77,85–89), nickel (75,79,90,91), niobium (92), rhodium (93,94), silver (95–97), tungsten (72,75–77,87,89), uranium (98), and vanadium (99). The coordination compounds formed from tertiary bismuthines are less stable than those formed from tertiary phosphines, arsines, or stibines.

Tertiary bismuthines appear to have a number of uses in synthetic organic chemistry (32), eg, they promote the formation of 1,1,2-trisubstituted cyclopropanes by the interaction of electron-deficient olefins and dialkyl dibromomalonates (100). They have also been employed for the preparation of thin films (qv) of superconducting bismuth strontium calcium copper oxide (101), as cocatalysts for the polymerization of alkynes (102), as inhibitors of the flammability of epoxy resins (103), and for a number of other industrial purposes.

Halobismuthines, Dihalobismuthines, and Related Compounds. Chloro-, dichloro-, bromo-, and dibromobismuthines are best prepared by the reaction of a tertiary bismuthine and bismuth trichloride or tribromide (7,43,45,46,104–107):

$$R_3Bi + 2\,BiX_3 \rightarrow 3\,RBiX_2$$

$$2\,R_3Bi + BiX_3 \rightarrow 3\,R_2BiX$$

Iodo- and diiodobismuthines are easily obtained by the reaction of the corresponding chloro-, dichloro-, bromo-, or dibromobismuthine with sodium or potassium iodide (107–110).

Several halo- and dihalobismuthines have been prepared by the partial alkylation or arylation of bismuth trichloride or tribromide with an organocadmium (111), organolead (112,113), organotin (114,115), or organozinc reagent (45). The reaction of a Grignard reagent with a bismuth trihalide usually leads to the formation of a tertiary bismuthine. In a few cases, however, it has been possible to isolate a halo- or dihalobismuthine from this type of reaction (116). Apparently, no fluoro- or difluorobismuthine has ever been isolated. The formation of bis(trifluoromethyl)fluorobismuthine *[124252-79-5]*, C_2BiF_7, by the interaction of tris(trifluoromethyl)bismuthine and iodine pentafluoride has, however, been suggested by ^{19}F nmr spectroscopy (117).

Halo- and dihalobismuthines are crystalline solids, most of which have melting points above 100°C. They are, in general, very reactive compounds and are decomposed by moisture, alcohols, and ammonia (118). Dialkylhalobismuthines are especially sensitive substances. They are spontaneously inflammable in air and may decompose even when water and oxygen are excluded. The diaryl compounds are more stable, but they should also be handled with caution. Some of them are powerful sternutators (119).

A number of compounds of the types $RBiY_2$ or R_2BiY, where Y is an anionic group other than halogen, have been prepared by the reaction of a dihalo- or halobismuthine with a lithium, sodium, potassium, ammonium, silver, or lead alkoxide (120,121), amide (122,123), azide (124,125), carboxylate (121,126), cyanide (125,127), dithiocarbamate (128,129), mercaptide (130,131), nitrate (108), phenoxide (120), selenocyanate (125), silanolate (132), thiocyanate (125,127), or xanthate (133). Dialkyl- and diarylhalobismuthines can also be readily converted to secondary bismuthides by treatment with an alkali metal (50,105,134):

$$R_2BiX + 2\,M \rightarrow R_2BiM + MX$$

Dibismuthines. Only about a dozen tetraalkyl- and tetraaryldibismuthines are known (135). These compounds can be obtained by the reaction of a sodium dialkyl- or diarylbismuthide and a 1,2-dihaloethane (66–69):

$$2\,R_2BiNa + XCH_2CH_2X \rightarrow R_2BiBiR_2 + CH_2{=}CH_2 + 2\,NaX$$

where X = Cl or Br. Several dibismuthines have also been obtained by the addition of the stoichiometric amount of sodium to a solution of a halobismuthine in liquid ammonia (105,136–139):

$$2\,R_2BiX + 2\,Na \rightarrow R_2BiBiR_2 + 2\,NaX$$

where X = Cl or I. The best method for the synthesis of tetraphenyldibismuthine *[7065-21-6]*, $C_{24}H_{20}Bi$, involves the reduction of diphenyliodobismuthine *[95825-92-6]*, $C_{12}H_{10}BiI$, using bis(cyclopentadienyl)cobalt(II) *[1277-43-6]*, $C_{10}H_{10}Co$, (140):

$$2(C_6H_5)_2BiI + 2\,Co(C_5H_5)_2 \rightarrow (C_6H_5)_2BiBi(C_6H_5)_2 + 2(C_5H_5)_2CoI$$

Dibismuthines tend to be thermally unstable. Thus tetramethyldibismuthine *[82783-70-8]*, $C_4H_{12}Bi_2$, decomposes at 25°C to yield trimethylbismuthine and metallic bismuth (66):

$$3(CH_3)_2BiBi(CH_3)_2 \rightarrow 4(CH_3)_3Bi + 2\,Bi$$

Tetraethyldibismuthine *[81956-27-6]*, $C_8H_{20}Bi_2$, undergoes a similar reaction at 40°C (67). At 0°C this dibismuthine as well as tetra-4-tolyldibismuthine *[114245-28-2]*, $C_{28}H_{28}Bi_2$, (105) decompose to form dark polymeric solids:

$$R_2BiBiR_2 \rightarrow R_3Bi + 1\,x(RBi)_x$$

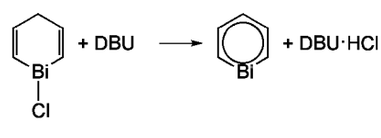
where R = C_2H_5 or 4-$CH_3C_6H_4$. Tetraphenyldibismuthine and 2,2′,5,5′-tetramethylbibismole *[88635-82-9]*, $C_{12}H_{1}\ Bi_2$, (71), however, are stable to 100°C. At 100°C the tetraphenyl compound decomposes to triphenylbismuthine and metallic bismuth (68).

Dibismuthines are very sensitive to oxidation. Thus tetramethyldibismuthine fumes in air, and tetraphenyldibismuthine in toluene solution rapidly absorbs oxygen. Under controlled conditions, dibismuthines react with chalcogens resulting in cleavage of the bismuth–bismuth bond and insertion of a chalcogen atom (105,138,140–142):

$$R_2BiBiR_2 + Y \rightarrow R_2BiYBiR_2$$

where Y = O, S, Se, or Te. Dibismuthines undergo a variety of other interesting reactions and have attracted considerable attention because a number of these substances are thermochromic (135).

Bismin and Its Derivatives. Bismin *[289-52-1]* (bismabenzene), C_5H_5Bi, the bismuth analogue of pyridine, has never been isolated, but it can be formed in solution by the dehydrohalogenation of 1-chloro-1,4-dihydrobismin *[39553-69-0]*, $C_5H_{}BiCl$, using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at low temperatures (114,143,144):



4-Methylbismin *[82995-62-8]*, $C_{}H_7Bi$, and 4-*tert*-butylbismin *[82995-64-0]*, $C_9H_{13}Bi$, have been obtained in solution by similar reactions. The presence of bismin and its 4-alkyl derivatives in these solutions has been demonstrated both by spectroscopy and via chemical trapping with 1,1,1,4,4,4-hexafluoro-2-butyne to yield Diels-Alder adducts. The potential aromaticity of the bismin ring system has aroused considerable interest and has been investigated with a variety of spectral methods. There seems to be little doubt that bismin does possess aromatic character.

Diarylbismuthinic Acids and Their Esters. Although organobismuth(V) compounds containing three, four, or five Bi–C bonds are well-known, no compounds containing two such bonds had been prepared until a number of methyl diarylbismuthinates (diarylmethoxybismuth oxides) were reported in 1988 (145).

$$ArBi + 4\text{-}CH_3C_6H_4SO_2NClNa \xrightarrow[CH_3OH]{C_6H_6} Ar_2Bi(O)OCH_3 + ArH + 4\text{-}CH_3C_6H_4SO_2NH_2 + NaCl$$

where Ar = C_6H_5, 4-$CH_3C_6H_4$, 3,4-$(CH_3)_2C_6H_3$, 1-naphthyl, or 4-CH_3-1-naphthyl. The yields varied from 10% (Ar = 4-$CH_3C_6H_4$) to 80% (Ar = 1-naphthyl and 4-CH_3-1-naphthyl). When Ar was 2-$CH_3C_6H_4$ the product was di-2-tolylbismuthinic acid *[124066-74-6]* rather than the ester. The reaction was unsuccessful when Ar was 4-ClC_6H_4, 3-$CF_3C_6H_4$, or 2-thienyl. The methyl esters underwent ester exchange when recrystallized from ethyl or isopropyl alcohols. Methyl diphenylbismuthinate *[124066-62-2]*, $C_{13}H_{13}BiO_2$, was readily hydrolyzed in water to diphenylbismuthinic acid *[124066-70-2]*.

Because organobismuth(V) compounds have found considerable use as oxidizing agents, the oxidizing ability of methyl di-1-naphthylbismuthinate *[124066-66-6]*, $C_{21}H_{17}BiO_2$, was investigated. Benzoin yields benzil, naphthalene, and metallic bismuth; hydrazobenzene yields azobenzene, and 1,1,2,2-tetraphenylethanediol yields benzophenone. 1,2-Diphenyl-1,2-ethanedione dihydrazone gives diphenylacetylene in 50% yield. Cyclohexane-1,2-diol and 1-phenylethane-1,2-diol, however, were unaffected.

Trialkyl- and Triarylbismuth Dihalides and Related Compounds. After the tertiary bismuthines, the triarylbismuth dihalides constitute the most important class of organobismuth compounds and are by far the largest class of compounds containing pentacovalent bismuth. However, only two trialkylbismuth dihalides have been prepared (146). These are *cis*-tripropenylbismuth dibromide *[66173-00-0]*, $C_9H_{15}BiBr_2$, and *trans*-tripropenylbismuth dibromide *[66212-22-4]*, $C_9H_{15}BiBr_2$, prepared by oxidative bromination of the corresponding bismuthines at 55°C. With most trialkylbismuthines studied to date, cleavage of one carbon–bismuth bond occurs on halogenation:

$$R_3Bi + X_2 \rightarrow R_2BiX + RX$$

By contrast, triarylbismuthines are readily chlorinated or brominated to the corresponding dichlorides or dibromides using chlorine or bromine. Other chlorinating agents include sulfur dichloride, sulfur monochloride, thionyl chloride, and iodine trichloride. Triarylbismuth difluorides have been prepared from the dichlorides by metathesis with potassium fluoride or by direct fluorination of triarylbismuthines with fluorine diluted with argon. No triarylbismuth diiodides are known. However, the two compounds triphenylbismuth iodide azide *[106112-77-0]*, $(C_6H_5)_3Bi(I)N_3$, and triphenylbismuth iodide isocyanate *[106112-78-1]*, $(C_6H_5)_3Bi(I)NCO$, have been prepared from triphenylbismuthine and iodine azide or iodine isocyanate, respectively (147). The triarylbismuth dihalides are stable crystalline solids with high melting points. X-ray studies, conductivities, and other physical measurements suggest that the bismuth atom in these compounds has trigonal–bipyramidal geometry.

In addition to the halides Ar_3BiX_2, a large number of compounds of the type Ar_3BiY_2, where Y is NO_3, N_3, CN, OCN, CH_3CO_2, CF_3CO_2, $1/2\ CO_3$, $1/2\ SO_4$, O_3SR, etc, can be prepared by metathesis from the dihalides and a silver, sodium, or potassium salt of the desired anion. The disulfonates $(C_6H_5)_3BI(O_3SR)_2$ have been prepared from the carbonate and the appropriate sulfonic acid (148). A number of mixed carbonates $Ar_2Ar'BiCO_3$, as well as mixed dichlorides $Ar_2Ar'BiCl_2$, have been prepared (149). Triphenylbismuth dicarboxylates have been obtained by several different methods including the following (150):

$$(C_6H_5)_3Bi + (CH_3)_3COOH + (RCO)_2O \rightarrow (C_6H_5)_3Bi(O_2CR)_2 + (CH_3)_3COH$$

The majority of the compounds of the type Ar_3BiY_2 are stable crystalline solids, soluble in organic solvents. They give normal molecular weights in solvents such as benzene.

Triphenylbismuth oxide *[7173-99-1]*, $C_{18}H_{15}BiO$, has been prepared from triphenylbismuth dicyanide *[41083-16-3]*, $C_{20}H_{15}BiN_2$, and mercuric oxide (151), and from triphenylbismuth dichloride and moist silver oxide (152). The ir and Raman spectra of this compound suggest that it is polymeric and has Bi–O–Bi bonds (153). Triphenylbismuth dihydroxide, $C_{18}H_{17}BiO_2$, and triarylbismuth hydroxide halides, eg, triphenylbismuth hydroxide chloride *[66214-57-1]*, $C_{18}H_{1}$ BiClO, have been reported in the earlier chemical literature. There is, however, no modern research on these types of compounds, and they may or may not exist.

In recent years organobismuth(V) compounds have found increasing use as reagents in organic synthesis. Thus they have been used for the oxidation of primary and secondary alcohols to the corresponding aldehydes (qv) and ketones (qv), for the oxidative cleavage of vicinal glycols (qv), and for the *O*-, *C*-, and *N*-arylation of a wide variety of organic compounds. Because most of these reactions occur under relatively mild conditions, organobismuth(V) reagents have proved to be of particular value when the substrates are sensitive natural products. Several review articles on this subject have been published (32,154–156), and a patent on the oxidation of steroidal, terpene, and sugar alcohols to the corresponding aldehydes (qv) and ketones (qv) has been issued (157) (see SUGAR ALCOHOLS). Although other types of organobismuth(V) compounds, Ar_4BiY and Ar_5Bi, have been used, the triaryl compounds Ar_3BiY_2 are the reagents of choice because of their ease of preparation and chemical stability.

In addition to use in organic synthesis, triarylbismuth dihalides and related compounds have found limited industrial use. A patent has been issued for the use of such compounds as antifungal agents on plastics or fibrous material (158). Compounds of the type $(C_6H_5)_3Bi(O_2CR)_2$, eg, triphenylbismuth dimethacrylate *[3371-98-0]*, $C_{2}H_{25}BiO_4$, and triphenylbismuth bis(4-vinylbenzoate) *[2181-48-8]*, $C_{3}H_{29}BiO_4$, are claimed to be effective agents against *Staphylococcus aureus* infections (159). Triphenylbismuth dichloride *[594-30-9]*, $C_{18}H_{15}BiCl_2$, is active against bean rust (160). Triarylbismuth dihalides have been used as catalysts for the carbonation of epoxides to form cyclic carbonates (161).

Quaternary Bismuth Compounds. Although earlier attempts had been made to prepare quaternary bismuth compounds, it was not until 1952 that tetraphenylbismuth bromide *[66173-02-2]*, $C_{24}H_{20}BiBr$, was obtained from pentaphenylbismuth *[3049-07-8]*, $C_{30}H_{25}Bi$, and one molar equivalent of bromine at 70°C (162):

$$(C_6H_5)_5Bi + Br_2 \rightarrow (C_6H_5)_4BiBr + C_6H_5Br$$

In a similar manner tetraphenylbismuth chloride *[42967-53-3]*, $C_{24}H_{20}BiCl$, (162) and tetraphenylbismuthonium tetrafluoroborate *[36682-02-7]*, $C_{24}H_{20}BBiF_4$, (163) are obtained from pentaphenylbismuth and hydrogen chloride or hydrogen tetrafluoroborate, respectively. When triphenylboron is used, the tetraphenylborate is obtained (162):

$$(C_6H_5)_5Bi + (C_6H_5)_3B \rightarrow [(C_6H_5)_4Bi]\,[(C_6H_5)_4B]$$

A number of other tetraarylbismuth compounds Ar_4BiY, where Y is a group, such as NO_3, ClO_4, OCN, N_3, etc, have been prepared from the chloride by metathesis. Two tetraalkylbismuth compounds have been reportedly prepared by means of the following synthesis (164):

$$(C_2H_5)_3Bi{\cdot}Al(C_2H_5)_3 + CH_3Cl \rightarrow [CH_3(C_2H_5)_3Bi]\,[(C_2H_5)_3AlCl]$$

$$[CH_3(C_2H_5)_3Bi]\,[(C_2H_5)_3AlCl] + NaBF_4 \rightarrow [CH_3(C_2H_5)_3Bi]BF_4 + (C_2H_5)_3Al + NaCl$$

When triphenylbismuth dichloride, in acetone, is treated with silver perchlorate, in absolute ethanol, tetraphenylbismuthonium perchlorate *[43047-28-5]*, $C_{24}H_{20}BiClO_4$, is formed (165). If, however, the same reaction is carried out only in acetone, the following reaction occurs (166):

$$(C_6H_5)_3BiCl_2 + 2\,AgClO_4 + (CH_3)_2CO \rightarrow [(C_6H_5)_3BiCH_2COCH_3]ClO_4 + 2\,AgCl + HClO_4$$

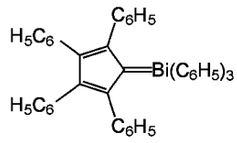
The corresponding tetrafluoroborate is obtained when silver tetrafluoroborate is used.

Quaternary bismuth compounds are generally unstable. When the anionic ligand is chloride or bromide, the compounds decompose spontaneously on standing; azides and selenocyanates decompose more rapidly. The perchlorates, tetrafluoroborates, and hexafluorophophates, however, are considerably more stable but eventually decompose. The vibrational spectra of the latter compounds show the presence of the free ion and are consistent with a tetrahedral BiC_4 skeleton for the cation. The acetonyltriphenyl compounds, $[(C_6H_5)_3BiCH_2COCH_3]Y$, where Y is ClO_4 or BF_4, also appear to be true bismuthonium salts.

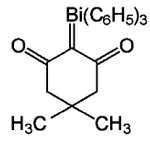
Quaternary bismuth compounds have not found extensive use in industry or in organic synthesis. In manifold studies of organobismuth(V) compounds as oxidizing and arylating agents, such quaternary bismuth compounds as $(C_6H_5)_4BiO_2CCH_3$, $(C_6H_5)_4BiO_3SC_6H_4CH_3$-4, and

$(C_6H_5)_4BiO_2CCF_3$ have been employed (32). There seems to be no marked advantage of the quaternary compounds over the more stable and more easily prepared compounds of the type Ar_3BiY_2.

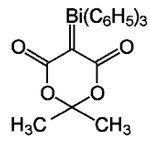
Bismuthonium Ylides. Prior to 1988 the only bismuthonium ylides known were (1) and (2).



(1)



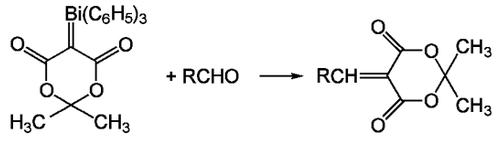
(2)



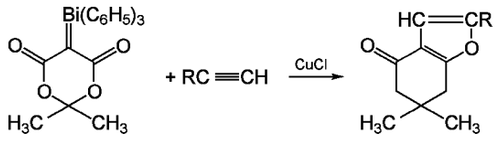
(3)

Structure (1) is an unstable blue solid which cannot be obtained in a pure state (167); structure (2) *[105071-90-7]*, however, is stable (168). Structure (2) was obtained from triphenylbismuth carbonate and dimedone. More recently a number of bismuthonium ylides, eg, (3) *[119016-81-8]* (169), have been prepared and their reactions studied.

Reactions of these compounds with phenylisothiocyanate and a number of aromatic and aliphatic aldehydes have been investigated (169,170). Only where R is $4\text{-}CH_3OC_6H_4$ or $C_6H_5CH{=}CH$ are the normal Wittig products obtained:

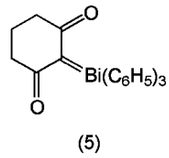


Using a number of other aldehydes, more complicated products result. Structure (2) was also found to react with alkynes in the presence of copper(I) chloride to give furans:



where R is C_6H_5, $4\text{-}CH_3C_6H_4$, $4\text{-}ClC_6H_5$, hexyl, and $C_6H_5COCH_2$. An excellent general method for the preparation of bismuthonium ylides from diazo compounds has been devised in which bis(hexafluoroacetylacetonato)copper(II) is employed as a catalyst (171). Two relatively stable ylides prepared by this procedure are (4) *[117968-30-6]* and (5) *[117968-31-7]*. The latter compound did not react with 2,4-dinitrobenzaldehyde.

$$(C_6H_5SO_2)_2C{=}Bi(C_6H_5)_3$$



(5)

Quinquenary Bismuth Compounds. No pentaalkylbismuth compounds have been reported, but a number of pentaarylbismuth compounds are known. Pentaphenylbismuth *[3049-07-8]*, $C_{30}H_{25}Bi$, was first prepared by means of the reaction (162):

$$(C_6H_5)_3BiCl_2 + 2\,C_6H_5Li \rightarrow (C_6H_5)_5Bi + 2\,LiCl$$

It can also be prepared by the reaction of phenyllithium with tetraphenylbismuth chloride or the *N*-triphenylbismuth derivative of 4-toluenesulfonamide (172):

$$4\quad CH_3C_6H_4SO_2N{=}Bi(C_6H_5)_3 + 2C_6H_5Li \rightarrow (C_6H_5)_5Bi + 4\quad CH_3C_6H_4SO_2NLi_2$$

Pentaphenylbismuth is a violet-colored, crystalline compound that decomposes spontaneously after standing for several days in a dry nitrogen atmosphere. With a variety of agents, eg, hydrohalic acids, halogens, and triphenylboron, one phenyl group is cleaved to form quaternary bismuth compounds.

The deep violet color of pentaphenylbismuth and certain other pentaarylbismuth compounds has been the subject of considerable speculation. It has been shown by x-ray diffraction (173) that the bismuth atom in pentaphenylbismuth is square–pyramidal. Well-formed crystals are dichromic, appearing violet when viewed in one plane but colorless in another plane. The nature of the chromophore has been suggested to be a charge-transfer transition by excitation of the four long equatorial bonds:

$$(C_6H_5)_4Bi{-}C_6H_5 \rightarrow (C_6H_5)_4Bi^{+}\ C_6H_5^{-}$$

In support of this suggestion, it has been shown that strong electron-withdrawing substituents on the aryl groups, which would make the charge-transfer transition more difficult, result in less highly colored compounds. Thus bis(pentafluorophenyl)triphenylbismuth *[111210-36-7]*, $C_{30}H_{15}BiF_{10}$, is an orange-colored solid. A number of pentaarylbismuth compounds that vary in color from violet, bis(4-fluorophenyl)tri-4-tolylbismuth *[124652-38-6]*, $C_{33}H_{29}BiF_2$, to yellow, bis(pentafluorophenyl)tri-4-tolylbismuth *[118798-77-9]*, $C_{33}H_{21}BiF_{10}$, have been prepared (174). Structures that could be determined by x-ray diffraction all exhibit square–pyramidal geometry.

Pentaphenylbismuth has been studied as a reagent in organic synthesis where it can act either as an oxidizing or an arylating agent. Thus it can be used for the oxidation of primary or secondary alcohols to aldehydes or ketones, respectively. Unlike compounds of the type Ar_3BiY_2 or Ar_4BiY that require the presence of a strong base for the oxidation of alcohols, pentaphenylbismuth oxidizes alcohols under neutral conditions. Thus benzyl alcohol is oxidized to benzaldehyde in 45% yield by pentaphenylbismuth; 3β-cholestanol gives the corresponding ketone in 70% yield. Pentaphenylbismuth can also act as an arylating agent. 2-Naphthol reacts to give 1-phenyl-2-naphthol in 61% yield (*C*-arylation), but phenol gives diphenyl ether in 42% yield (*O*-arylation). Often both oxidation and phenylation occur. Thus estradiol gives a mixture of 2,4-diphenylestrone, 4-phenylestrone, and 2,4-diphenylestradiol. When 2-phenylethanol is treated with pentaphenylbismuth, triphenylacetaldehyde is produced in 69% yield.

Bismuth Compounds Used in Medicine

Therapeutic properties were first attributed to bismuth during the seventeenth century, and bismuth compounds were tried for the treatment of both syphilis and gonorrhea before the end of the eighteenth century (118). During the 1920s, it was shown that bismuth compounds were comparable in efficacy to the best antisyphilic drugs then available (175). During the next quarter of a century, bismuth compounds became widely used as adjuncts to the arsenical therapy of syphilis (176). However, antibiotics (qv), especially penicillin, have made both arsenic and bismuth compounds completely obsolete for the treatment of this disease (177,178).

Bismuth compounds were once employed for the treatment of amoebic dysentery, certain skin diseases, and several spirochetal diseases besides syphilis, but these substances are now seldom considered the drugs of choice. Various insoluble preparations of bismuth, especially the subcarbonate, subnitrate, subgallate, subcitrate, and subsalicylate, are still employed for the treatment of ulcers and other gastrointestinal disorders, even though use for these purposes is often supported largely by tradition. With a few possible exceptions, it is now difficult to justify the presence of bismuth compounds in a modern therapeutic armamentarium. A review of the biological activity of organobismuth compounds has been published (179).

Bismuth subsalicylate *[14882-18-9]*, Pepto-Bismol, is a basic salt of varying composition, corresponding approximately to *o*-HOC H_4CO_2(BiO). Like a number of other insoluble bismuth preparations, it is not currently approved in the United States for the treatment of peptic ulcer disease but is under active investigation for this purpose (180). It does appear to be effective for the relief of mild diarrhea and for the prevention of travelers' diarrhea (181). The ready availability of this drug, however, may lead to its overuse and result in toxic effects caused by both the salicylate and bismuth components. It has been suggested that bismuth subsalicylate is somewhat effective in the symptomatic treatment of isosporiasis, a disease caused by the intracellular parasite *Isospora belli* (182).

Bismuth subcarbonate *[5892-10-4]* (basic bismuth carbonate) is a white or pale yellow powder that is prepared by interaction of bismuth nitrate and a water-soluble carbonate. The exact composition of this drug depends on the conditions of precipitation; it corresponds approximately to the formula $(BiO)_2CO_3$. It has been widely used as an antacid (183).

Tripotassium dicitratobismuthate *[57644-54-9]* (bismuth subcitrate), De-Nol is a buffered aqueous suspension of a poorly defined, water-insoluble bismuth compound. It is said to very effective for the treatment of gastric and duodenal ulcers (180,184). There have not yet been any reports of bismuth encephalopathy following the use of this drug.

Bismuth subnitrate *[1304-85-4]* (basic bismuth nitrate) can be prepared by the partial hydrolysis of the normal nitrate with boiling water. It has been used as an antacid and in combination with iodoform as a wound dressing (183). Taken internally, the subnitrate may cause fatal nitrite poisoning because of the reduction of the nitrate ion by intestinal bacteria.

Bismuth subgallate *[12552-60-2]* (basic bismuth gallate), Dermatol, is a bright yellow powder that can be prepared by the interaction of bismuth nitrate and gallic acid in an acetic acid medium. It has been employed as a dusting powder in some skin disorders and as an ingredient of suppositories for the treatment of hemorrhoids (183,185). It has been taken orally for many years by colostomy patients in order to control fecal odors, but the drug may cause serious neurological problems (186).

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BISPHENOL A.

See ALKYLPHENOLS; POLYCARBONATES.

BITUMENS.

See ASPHALT; ROOFING MATERIALS.

BLACK POWDER.

See EXPLOSIVES AND PROPELLANTS; PYROTECHNICS.

BLANC FIXE.

See BARIUM COMPOUNDS.

BLEACHING.

See PULP.

BLEACHING AGENTS

Survey,
Pulp and Paper,

SURVEY

A bleaching agent is a material that lightens or whitens a substrate through chemical reaction. The bleaching reactions usually involve oxidative or reductive processes that degrade color systems. These processes may involve the destruction or modification of chromophoric groups in the substrate as well as the degradation of color bodies into smaller, more soluble units that are more easily removed in the bleaching process. The most common bleaching agents generally fall into two categories: chlorine and its related compounds (such as sodium hypochlorite) and the peroxygen bleaching agents such as hydrogen peroxide and sodium perborate. Reducing bleaches represent another category. Bleaching agents are used for textile, paper, and pulp bleaching as well as for home laundering.

The History of Bleaching

Textile Bleaching. There is evidence of chemical bleaching of cloth prior to 300 BC (1). Soda ash prepared from the burning of seaweed was used to clean the cloth followed by souring, ie, treatment with soured milk to neutralize the alkalinity remaining on the cloth. The cloth was then exposed to the sun to complete the bleaching process. Sun bleaching, which became known as crofting, occurred over a matter of weeks during which time the cloth was kept moist to enhance the bleaching process (2). During the eighteenth century improvements were developed including the use of sulfuric acid in the souring process and the use of lime in the cleaning process, though crofting still required large tracts of primarily coastal land. With the onset of mechanized weaving, the production of cloth was outstripping the availability of land, which set the stage for the introduction of chemical bleaching.

Scheele, a Swedish chemist, discovered chlorine gas in 1784 and demonstrated its use in decolorizing vegetable dyes. Berthollet first produced solutions of hypochlorite by combining chlorine gas with alkalies and suggested using the gas for bleaching. A Scottish bleacher followed the suggestion and introduced chlorine into a bleach works in Glasgow. The efficiency of the process lead to its widespread use, though the low pH resulted in fabric damage and worker health problems. Two chemists, Valette and Tennant, developed chlorinated lime solutions that minimized these difficulties.

Tennant received a patent in 1799 for bleaching powder formed by the absorption of chlorine gas by dry hydrate of lime. Although this eliminated the need for on-site manufacture of chlorine, evidence suggests its use by bleachers caught on slowly. The bleaching powder was the chief source of textile bleaches over the next century and was the impetus for much of the early chemical and chemical engineering developments. Tropical bleach was developed by the addition of quicklime to bleaching powder to make a material suitable for use under tropical conditions. After World War I, technology for shipping liquid chlorine and caustic economically was developed allowing for the on-site manufacture of sodium hypochlorite solutions at the textile mills. As a result, use of bleaching powder diminished.

After World War I, other chlorine-based bleaches were developed. In 1921 the use of chlorine dioxide for bleaching fibers was reported followed by the development of the commercial process for large-scale production of sodium chlorite. In 1928 the first dry calcium hypochlorite containing 70% available chlorine was produced in the United States. This material largely replaced bleaching powder as a commercial bleaching agent.

Although hydrogen peroxide was prepared as early as 1818 by Thenard, the peroxides received little use as textile bleaches. Hydrogen peroxide was first prepared by the action of dilute sulfuric acid on barium peroxide, but later sodium peroxide and dilute acids were used. The prices of peroxides were high initially, and they found use only as a specialty chemical. Electrolytic methods in the 1920s allowed for the synthesis of less costly, strong (ca 30%) solutions of hydrogen peroxide. By 1930, hydrogen peroxide was being used to bleach cotton goods, wool, and silk on a limited scale. Shortly thereafter, the J-Box was developed by the FMC Corp. allowing for continuous bleaching of textiles with hydrogen peroxide (3). By 1940, 65% of all cotton bleaching was done with hydrogen peroxide.

Pulp Bleaching. The development of pulp bleaching parallels textile bleaching in many respects partially because early paper was generally made from rags. In the 1700s, sunlight was used to bleach paper. After the turn of the century, bleaching powder was used to whiten the rags used to make paper. During the nineteenth century wood began to be used as a source of paper and sulfite pulping was developed. Although the Kraft process was discovered not long after, the sulfite process dominated for many years, since it yielded a whiter more easily bleached pulp. Calcium hypochlorite continued to be the bleaching agent used but multistage bleaching processes began to be employed. After World War I, compressed chlorine gas became available and its well-established properties as a delignifying agent ultimately resulted in its use in a chlorine-caustic extraction-hypochlorite (CEH) bleaching sequence. By the 1950s chlorine dioxide generators were developed leading to the extensive use of this chemical as a bleaching agent particularly for the hard to bleach Kraft pulp. More recently peroxygens, particularly hydrogen peroxide, have been utilized (see BLEACHING AGENTS, PULP AND PAPER).

Household and Commercial Laundering. Prior to the turn of the twentieth century home bleaching in the United States was accomplished by the same method used by the ancient Romans and Gauls. Clothes were laundered in a mildly alkaline bath and then subjected to sunlight bleaching. In the period from 1910 to 1920, 5.25% sodium hypochlorite solutions were developed and distributed regionally in the United States. By the mid-1930s these solutions were available nationwide. This formula has remained essentially unchanged since its initial introduction. In the 1950s laundry products containing dry sources of hypochlorite were introduced into the United States. However, by the late 1960s the dry chlorine products had disappeared probably because of lower efficacy compared to liquid hypochlorite and fabric damage resulting from placement of the product on wet fabric. In Europe, laundry detergents containing sodium perborate as a bleaching agent were introduced in the early 1900s (4). The perborate dissolves during the laundering process and releases hydrogen peroxide. Sodium perborate continues to be heavily used in European laundry detergents because of the high (up to 95°C) wash temperatures. In the 1950s laundry products containing sodium perborate were introduced in the United States. In the late 1970s tetraacetylethylenediamine (TAED), a perborate activator, was introduced into European detergents. TAED with perborate generates peracetic acid in the wash, which is more effective than hydrogen peroxide. TAED is currently contained in over 50% of European detergents (5). In the United States in 1982 a dry bleach containing diperoxydodecanedioic acid was test marketed but not expanded. In the late 1980s a detergent product containing the perborate activator nonanoyloxybenzene sulfonate was introduced. This activator generates pernonanoic acid when combined with hydrogen peroxide generated from sodium perborate monohydrate.

Commercial laundries have used and continue to use sodium hypochlorite as the primary bleaching agent because of its whitening and disinfectant properties.

The Chemistry of Bleaching Compounds

CHLORINE-CONTAINING BLEACHING AGENTS

Chlorine-containing bleaching agents are the most cost-effective bleaching agents known. They are also effective disinfectants, and water disinfection is often the largest use of many chlorine-containing bleaching agents. They may be divided into four classes: chlorine, hypochlorites, *N*-chloro compounds, and chlorine dioxide.

The first three classes are called available chlorine compounds and are related to chlorine by the equilibria in equations 1–4. These equilibria are rapidly established in aqueous solution (6), but the dissolution of some hypochlorite salts and *N*-chloro compounds can be quite slow.

$$Cl_2\ (gas) \rightleftharpoons Cl_2\ (aqueous)$$

(1)

$$Cl_2\ (\text{aqueous}) + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$$

(2)

$$HOCl \rightleftharpoons H^+ + OCl^-$$

(3)

$$RR'NCl + H_2O \rightleftharpoons HOCl + RR'NH$$

(4)

The total concentration or amount of chlorine-based oxidants is often expressed as available chorine or less frequently as active chlorine. Available chlorine is the equivalent concentration or amount of Cl_2 needed to make the oxidant according to equations 1–4. Active chlorine is the equivalent concentration or amount of Cl atoms that can accept two electrons. This is a convention, not a description of the reaction mechanism of the oxidant. Because Cl_2 only accepts two electrons as does HOCl and monochloramines, it only has one active Cl atom according to the definition. Thus the active chlorine is always one-half of the available chlorine. The available chlorine is usually measured by iodometric titration (7,8). The weight of available chlorine can also be calculated by equation 5.

$$\text{weight available chlorine} = 70.9 \times \text{moles of oxidant} \times \frac{\text{number active Cl atoms}}{\text{molecule}} \times x$$

(5)

where 70.9 represents the mol wt of Cl_2 and moles of oxidant can be represented wt oxidant mol wt of oxidant.

In solutions, the concentration of available chlorine in the form of hypochlorite or hypochlorous acid is called free-available chlorine. The available chlorine in the form of undissociated *N*-chloro compounds is called combined-available chlorine. Several analytical methods can be used to distinguish between free- and combined-available chlorine (8). Bleaches that do not form hypochlorite in solution like chlorine dioxide and nonchlorine bleaches can be characterized by their equivalent available chlorine content. This can be calculated from equation 5 by substituting the number of electrons accepted divided by two for the number of active chlorine atoms. It can also be measured by iodometric titration.

The actual form of an available chlorine bleach in solution must be determined from equations 1–4. The equilibrium constants for equations 2 and 3 are $3.94 \times 10^{-4}\ M^2$ (9) and $2.88 \times 10^{-8}\ M$ (10) at 25°C, respectively. Thus, above pH 9.5 more than 99% of the available chlorine is present as hypochlorite ions. The ratio of hypochlorous acid to hypochlorite ion increases with decreasing pH until pH 5.5, below which less than 1% of the available chlorine will be hypochlorite ions. Below pH 6, Cl_2 may be present. Its amount increases with decreasing pH and increasing total available chlorine. With an available chlorine concentration of 0.1%, Cl_2 begins to appear about pH 4 and becomes dominant about pH 2.5. At an available chlorine concentration of 10%, Cl_2 appears about pH 6, and becomes dominant about pH 4.5. Figure 1 shows the distribution of available chlorine species as a function of pH in an aqueous solution of 0.5% available chlorine. Other species that may be present in insignificant amounts are Cl_3^-; from Cl_2 (aq) and H_2OCl^+ and Cl_2O from HOCl (11).

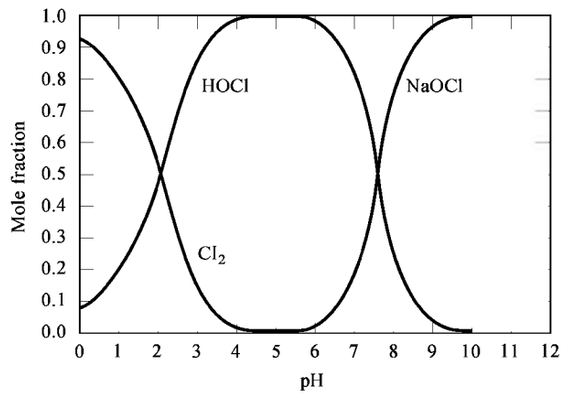


Fig. 1. Distribution of 0.5 wt % available chlorine with equimolar chloride at 25°C in a closed system.

With *N*-chloro compounds, the species in solution also depends on their individual hydrolysis constants as shown in equation 4. Those with larger constants allow a higher hypochlorite concentration, which usually gives stronger bleaching because *N*-chloro compounds are weaker oxidants than hypochlorite (see CHLORAMINES AND BROMAMINES). Although *N*-chloro compounds react quickly with other *N*-compounds and may remove some stains faster than hypochlorite (12), the undissociated *N*-chloro compound usually serves as a reservoir to replenish hypochlorite as it is consumed. This reduces reactivity compared to the higher hypochlorite concentration required to deliver the same amount of available chlorine (13–15). Stability of the available chlorine may also be improved (16,17). Even when the *N*-chloro compound completely dissociates at the use concentration, it can reduce the hypochlorite concentration in a concentrated solution or product. This may reduce the damage done by spills, improve stability, or allow the use of a wider variety of ingredients. *N*-Chloro compounds may also be formed *in situ* as when *N*-compounds are used in dry compositions with active chlorine compounds to scavenge free hypochlorite to protect other materials (18,19).

Solutions of available chlorine bleaches decompose on standing at a rate that depends on the conditions described below. Hypochlorous acid *[7790-92-3]* and hypochlorite anions decompose according to equations 6 and 7 (20,21):

$$3\ HOCl \rightarrow HClO_3 + 2\ HCl$$

(6)

$$3\ OCl^- \rightarrow ClO_3^- + 2\ Cl^-$$

(7)

The solutions are most stable above pH 11 where the decomposition rate is nearly independent of pH. In this region, the decomposition rate has a second-order dependence on the concentration of hypochlorite. It also increases with increasing ionic strength. Thus concentrated solutions decompose much faster than dilute solutions. Because of an unusually high activation energy, the decomposition rate increases greatly with temperature. Nevertheless, solutions with less than about 6% available chlorine and a pH above 11 have acceptable long-term stability below about 30°C.

Below pH 11, the decomposition rate becomes dependent on pH and the mechanism becomes more complicated. The rate increases greatly as the

pH decreases from 11 to 7 where the rate reaches a maximum. As the pH decreases from 7 to 3, the rate decreases. Below about pH 3 the rate becomes reasonably slow but still considerably faster than at pH 11. The mechanisms are not well known, and they may be different in each of these pH ranges. In all cases, the decomposition rate increases greatly with temperature and with a second- or higher-order dependence on the concentration of hypochlorous acid and or hypochlorite.

Decomposition also occurs by equation 8, which can usually be ignored unless it is catalyzed by transition-metal ions (22,23):

$$2\,OCl^- \rightarrow O_2 + 2\,Cl^- \tag{8}$$

Even very small amounts of transition-metal ions like cobalt, nickel, and copper cause rapid decomposition. They form reactive intermediates that can decrease the stability of oxidizable compounds in the bleach solution and increase the damage to substrates. Hypochlorite is also decomposed by uv light (24,25). Acidic solutions also lose available chlorine by the reverse of equations 1 and 2.

Commercially important solid available chlorine bleaches are usually more stable than concentrated hypochlorite solutions. They decompose very slowly in sealed containers. But most of them decompose quickly as they absorb moisture from air or from other ingredients in a formulation. This may release hypochlorite that destroys other ingredients as well.

Chlorine. Except to bleach wood pulp and flour, chlorine *[7782-50-5]* itself is rarely used as a bleaching agent. Chlorine is almost always first converted into one of the bleaching agents described, and they are almost always used at a pH where Cl_2 is not present. However, it has been the practice to use acid chlorination where Cl_2 is the active species in the first step of pulp bleaching. Since chlorine reacts primarily by chlorination, large amounts of chlorinated organic by-products are formed (26). Environmental concerns about discharging these by-products in waste effluents are rapidly changing this process (27–29).

Hypochlorites.

Sodium Hypochlorite. The principal form of hypochlorite produced is sodium hypochlorite *[7681-52-9]*, NaOCl. It is invariably made and used as an aqueous solution and is usually prepared by the chlorination of sodium hydroxide solutions as shown in equation 9, though other bases such as sodium carbonate can be used (30).

$$Cl_2 + 2\,NaOH \rightleftharpoons NaOCl + NaCl + H_2O \tag{9}$$

Chlorine gas is usually used, but electrolysis of alkaline salt solutions in which chlorine is generated *in situ* is also possible and may become more important in the future. The final pH of solutions to be sold or stored is always adjusted above 11 to maximize stability. The salt is usually not removed. However, when the starting solution contains more than 20.5% sodium hydroxide some salt precipitates as it is formed. This precipitate is removed by filtration to make 12–15% NaOCl solutions with about one-half of the normal amount of salt. Small amounts of such solutions are sold for special purposes. Solutions with practically no salt can be made by reaction of high purity hypochlorous acid with metal hydroxides.

A 5–6% sodium hypochlorite solution is sold for household purposes, of which the largest use is in laundry. Solutions of 10–15% NaOCl are sold for swimming pool disinfection, institutional laundries, and industrial purposes. Solutions of various strengths are used in household and industrial and institutional (I & I) cleaners, disinfectants, and mildewcides. A small amount is used in textile mills. Sodium hypochlorite is also made on site with 30–40 g L available chlorine for pulp bleaching, but its use is decreasing in order to reduce chloroform emissions (see CHLORINE OXYGEN ACIDS AND SALTS).

Calcium Hypochlorite. The principal form of solid hypochlorite produced commercially is calcium hypochlorite *[7778-54-3]*, $Ca(OCl)_2$. It decomposes rapidly and exothermically gives off oxygen and chlorine monoxide gases when heated above 175°C. It also reacts vigorously or explosively with oxidizable materials. The most common form contains 6–12% water and 65% available chlorine. The water reduces the risk of self-sustained decomposition because of organic contaminants or ignition. The older variety contains about 1% water and 70–74% available chlorine. Both forms also contain sodium chloride *[7647-14-5]* and small amounts of calcium hydroxide *[1305-62-0]*, calcium chloride *[10043-52-4]*, calcium chlorate *[10137-74-3]*, and calcium carbonate *[471-34-1]*. They are made by chlorination of hydrated lime (calcium hydroxide) in a way that minimizes the amounts of unwanted salts. The resulting product contains much fewer insoluble materials and is more stable than bleaching powder.

The largest use of calcium hypochlorite is for water treatment. It is also used for I & I and household disinfectants, cleaners, and mildewcides. Most of the household uses have been limited to in-tank toilet bowl cleaners. In areas where chlorine cannot be shipped or is otherwise unavailable, calcium hypochlorite is used to bleach textiles in commercial laundries and textile mills. It is usually first converted to sodium hypochlorite by mixing it with an aqueous solution of sodium carbonate and removing the precipitated calcium carbonate. Or, it can be dissolved in the presence of sufficient sodium tripolyphosphate to prevent the precipitation of calcium salts. However, calcium hypochlorite is not usually used to bleach laundry and textiles because of problems with insoluble inorganic calcium salts and precipitation of soaps and anionic detergents as their calcium salts.

Bleach Liquor. Bleach liquor or lime bleach liquor is an aqueous solution of calcium hypochlorite and calcium chloride. It typically contains 30–35 g L of available chlorine, though it may be as high as 85 g L. It has been used in pulp bleaching, when it can be made more cheaply than sodium hypochlorite. It is prepared on site by chlorinating lime solutions.

Bleaching Powder and Tropical Bleach. Bleaching powder *[64175-94-6]*, also known as chlorinated lime and chloride of lime, is an indefinite, complex mixture of calcium hypochlorite, calcium hydroxide, calcium chloride, and their hydrates. The proportions of these species vary with the manufacturer as does the available chlorine, which usually ranges between 24% and 37%. It is usually made by chlorinating slightly moist hydrated lime (calcium hydroxide). It has also been made by chlorinating a slurry or solution of calcium chloride (31). Bleaching powder readily decomposes in moist air through the absorption of water and carbon dioxide. Its stability can be improved by adding calcium oxide. Since this is needed especially in hot, humid climates, such mixtures are known as tropical bleach, super tropical bleach, or stabilized tropical bleach. They typically contain 15% to 30% available chlorine.

Historically, bleaching powder and tropical bleach were significant sources of available chlorine but very little are used today. This is because of the greater availability of sodium hypochlorite solutions and the development of calcium hypochlorite. They are still used to sanitize fields, drainage ditches, and reservoirs where its insoluble portion is not important. And, they are important sources of available chlorine within some less developed tropical countries.

Dibasic Magnesium Hypochlorite. This salt $Mg(OCl)_2 \cdot 2Mg(OH)_2$, *[11073-21-5]*, is safer than calcium hypochlorite because of its higher thermal stability and its endothermic rather than exothermic decomposition. Its preparation as a solid with 50–58% available chlorine is patented (32,33) but not sold commercially.

Lithium Hypochlorite. Commercial lithium hypochlorite *[13840-33-0]*, LiOCl, is a solid with about 35% available chlorine. It is made from concentrated solutions of sodium hypochlorite and lithium chloride. It consists of 30% lithium hypochlorite and various other salts (34).

Lithium hypochlorite is used in I & I laundry detergents and I & I dry laundry bleaches. Like sodium hypochlorite, it does not precipitate soaps and other anionic detergents. However, lithium hypochlorite is an expensive source of available chlorine and not much is used for bleaching. Its principal use is as a shocking agent for swimming pool disinfection.

Chlorinated Trisodium Phosphate. Chlorinated trisodium phosphate *[11084-85-8]* is a crystalline complex of hydrated trisodium orthophosphate and sodium hypochlorite that releases hypochlorite when mixed with water. Its formula is $(Na_3PO_4 \cdot 11H_2O)_4 \cdot NaOCl$. Commercial products have 3.5–3.7% available chlorine. They are probably a mixture of phosphate salts, and they contain some sodium chloride.

The use of chlorinated trisodium phosphate is declining. It has been largely replaced by chlorinated isocyanurates in powdered abrasive cleansers and automatic dishwash detergents to reduce cost, improve performance, or comply with restrictions on the use of phosphates. Some chlorinated trisodium phosphate is still used in commercial laundries and in disinfectant cleaners.

Hypochlorous Acid. Hypochlorous acid *[7790-92-3]* solutions are made for immediate use as chemical intermediates from chlorine monoxide or in bleaching and water disinfection by adjusting the pH of hypochlorite solutions. Salt-free hypochlorous acid solutions have been economically made

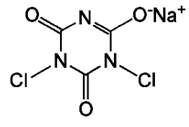
from steam and chlorine (35). These solutions may have sufficient stability at 0°C to be sold for industrial use.

Oxidation of Chlorides. Hypochlorite can also be formed by the *in situ* oxidation of chloride ions by potassium peroxymonosulfate *[25482-78-4]* (36). Ketones like acetone catalyze the reaction (37). The triple salt of potassium peroxymonosulfate is a stable powder that has been combined with chloride salts and sold as toilet bowl cleaners. Bromides can be used in place of chlorides to form hypobromites, and such combinations are used to disinfect spas and hot tubs.

Hypobromites. The chemistry of hypobromite is similar to hypochlorite. It reacts faster than hypochlorite and gives better bleaching at higher pH and lower temperatures. It also decomposes according to equations 6 and 7 much faster than hypochlorite. The most stable solutions decompose quickly and must be freshly prepared. This can be done by adding a bromide salt to a hypochlorite solution, since hypochlorite oxidizes bromide to hypobromite. Usually a catalytic amount of bromide is used since much of it will be regenerated as the hypobromite is reduced during bleaching (38). Dry compositions containing a bromide salt and a solid available chlorine compound can also be used (39). A few *N*-bromo compounds are also available.

N-Chloro Compounds.

Chlorinated Isocyanurates. The principal solid chlorine bleaching agents are the chlorinated isocyanurates. The one used most often for bleaching applications is sodium dichloroisocyanurate dihydrate *[51580-86-0]* with 56% available chlorine. It is the most water-soluble, the fastest to dissolve, and the least hazardous. It has good stability and compatibility with other dry ingredients. Anhydrous sodium *[2893-78-9]* (1) and potassium *[2244-21-5]* salts with 63% and 59% available chlorine are also available. The potassium salt is less soluble in water and is claimed to have the best stability in dry products containing other ingredients (40). Trichloroisocyanuric acid *[87-90-1]* (2) with 90% available chlorine is the most economical and the one used most often for water disinfection. Not much is used for bleaching because it dissolves slowly and has poor stability in dry products containing other ingredients. It also decomposes with moisture to give off explosive nitrogen trichloride gas.



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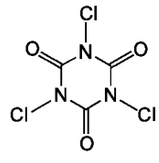

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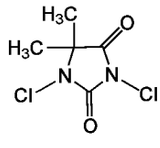
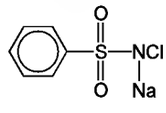


(3)

Halogenated Hydantoins. These are stable solids with limited use as bleaches. They dissolve too slowly to use in household laundry and automatic dishwashing. 1,3-Dichloro-5,5-dimethylhydantoin *[118-52-5]* (3) is sold with 65–75% available chlorine. It is used as a bleach in hospital and other industrial laundries and in disinfectant cleaners. Some 1-bromo-3-chloro-5,5-dimethylhydantoin *[6079-88-2]* is also used. It is a more effective bleach and disinfectant at lower temperatures and higher alkalinities than 1,3-dichloro-5,5-dimethylhydantoin because it hydrolyzes to hypobromite.

Other N-Chloro Compounds. Sodium *N*-chlorobenzenesulfonamide (chloramine B) *[127-52-6]* (4), sodium *N*-chloro-*p*-toluenesulfonamide (chloramine T) *[127-65-1]* (5), *N*-chlorosuccinimide *[128-09-6]* (6), and trichloromelamine *[12379-38-3]* (7) have also had minor roles as bleaching agents.



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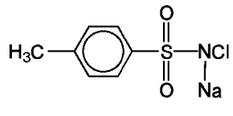

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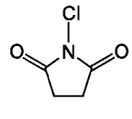

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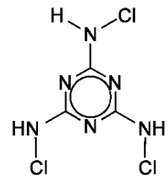


(7)

They are mainly sold as disinfectants, because they display poor bleaching as a result of low hydrolysis constants or poor solubility. *N*-Chloro compounds with low hydrolysis constants like chloramine T can be used to boost the bleaching of peroxide laundry bleaches (41–44). The bleaching remains inferior to using sodium hypochlorite laundry bleach, however. Tetrachloroglycoluril *[776-19-2]* (45) sodium trichlorometaphosphimate *[67651-15-14]* (46), sodium *N*-chloroimidodisulfonate *[67700-32-7]* (47), 1,3-dichlorotetrahydroquinazoline-2,4-dione *[23767-45-5]* (48,49), and *N*-chlorophenylbiquanidino compounds (50,51) have been unsuccessfully marketed as bleaching agents. Many other *N*-chloro compounds have been patented as bleaching agents, the most notable are mono- *[17172-27-9]* and dichlorosulfamic acid *[17085-87-9]* (52–54).

Chlorine Dioxide. Chlorine dioxide *[10049-04-4]*, ClO_2, is a gas that is more toxic than chlorine. It can explode at concentrations greater than 10% in air. The liquid boils at 11°C but explodes above 40°C. It can be stored and transported as its octahydrate if kept frozen, but almost all chlorine dioxide is made on site for immediate use. Large amounts for pulp bleaching are made by several processes (55,56) in which sodium chlorate *[7775-09-9]* is reduced with chloride, methanol, or sulfur dioxide in highly acidic solutions by complex reactions. For most other purposes chlorine dioxide is made from sodium chlorite *[7758-19-2]*. Acidic solutions of sodium chlorite are oxidized by chlorine as in equation 10:

$$2\,NaClO_2 + Cl_2 \rightarrow 2\,NaCl + 2\,ClO_2 \tag{10}$$

Hypochlorous acid can also be used, but the reaction is slower. Chlorine dioxide is also made by adding acid to sodium chlorite solutions by the overall reaction in equation 11:

$$5\,NaClO_2 + 4\,HCl \rightarrow 4\,ClO_2 + 5\,NaCl + 2\,H_2O \tag{11}$$

Some chlorine and chlorate also form through competing reactions. Chlorine dioxide is also evolved from mixtures of powdered sodium chlorite and acidic clays or alumina.

The reactivity of acidified chlorite solutions is reduced for bleaching some textiles by adding compounds like polyamines, pyrophosphates, and hydrogen peroxide that suppress the formation of chlorine dioxide (57). Another method is to buffer the solution at pH 5–6 to reduce the rate of chlorine dioxide formation. Hydrolysis of anhydrides and esters or oxidation of alcohols can be used to slowly generate acids to promote chlorine dioxide formation (58). Aldehydes also promote chlorine dioxide generation from neutral chlorite solutions, but the effect is greater than simply lowering the pH as they oxidize to acids (59).

Chlorine dioxide is usually used in aqueous solution. It is a weaker oxidant than hypochlorite. Unlike chlorine it does not react with water to form hypochlorite or with amines to form *N*-chloro compounds. Thus chlorine dioxide is easily removed from solutions by passing air through the solution or its headspace. Chlorine dioxide solutions decompose by equation 12:

$$2\,ClO_2 + 2\,NaOH \rightarrow NaClO_2 + NaClO_3 + H_2O \tag{12}$$

This reaction is very slow in acid but rapid above pH 10. Chlorine dioxide solutions are also decomposed by light.

The biggest use of chlorine dioxide is in bleaching wood pulp. In some mills, much of the chlorine and hypochlorite has been replaced by chlorine dioxide to reduce the amount of chlorinated by-products. Chlorine dioxide is also used to bleach textiles, flour, and edible fats and oils.

PEROXYGEN COMPOUNDS

Peroxygen compounds contain the peroxide linkage (—O—O—) in which one of the oxygen atoms is active. This activity, referred to as active oxygen (AO), is measured by the oxidation of iodide to iodine under acidic conditions or by a ceric sulfate titration (60). Active oxygen content, usually expressed as a percent, is the atomic weight of active oxygen divided by the molecular weight of the compound (eq. 13):

$$\text{active oxygen, \%} = 100 \times \frac{\text{number of active oxygens} \times 16}{\text{mol wt of compound}} \tag{13}$$

Hydrogen Peroxide. Hydrogen peroxide *[7722-84-1]* is one of the most common bleaching agents (see HYDROGEN PEROXIDE). It is the primary bleaching agent in the textile industry, and is also used in pulp, paper, and home laundry applications. In textile bleaching, hydrogen peroxide is the most common bleaching agent for protein fibers, and is also used extensively for cellulosic fibers.

Pure hydrogen peroxide has an active oxygen content of 47%. It is the least expensive source of active oxygen commercially available. Moreover, it is a liquid, making it convenient for many bleaching applications. Hydrogen peroxide is usually sold in solutions containing 30–35%, 50% or 65–70 wt % of the active material. More concentrated solutions (80–85%, 90%) are available in limited quantities. Concentrated solutions of hydrogen peroxide are hazardous and must be handled with extreme care (61).

Hydrogen peroxide is a very weak acid and in aqueous solutions only dissociates slightly (eq. 14); $K_a = 1.78 \times 10^{-12}$. Undissociated hydrogen peroxide is relatively stable, and for this reason all commercial products are adjusted to an acid pH (62).

$$H_2O_2 \rightleftharpoons H^+ + HO_2^- \tag{14}$$

A considerable amount of energy is liberated when hydrogen peroxide undergoes decomposition to oxygen and water (eq. 15): $\Delta H_{25°C} = -94.64$ kJ/mol (−22.62 kcal/mol); activation energy = 209 kJ/mol (50 kcal/mol).

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2 \tag{15}$$

This decomposition may be considered a self-oxidation and occurs most rapidly in basic solutions. Decomposition of hydrogen peroxide is also greatly accelerated in the presence of heavy metals and easily oxidizable substances (63). The presence of low concentrations of heavy metals (such as Fe and Cu) in hydrogen peroxide can increase the rate of decomposition by many orders of magnitude over the entire pH range for typical uses. Therefore, commercial hydrogen peroxide solutions are stabilized with additives that provide protection against decomposition (64–68). Typically these additives are metal chelating agents that bind free metal ions and significantly reduce the catalytic rate of decomposition.

Hydrogen peroxide bleaching is performed in alkaline solution where part of the hydrogen peroxide is converted to the perhydroxyl anion (eq. 14).

The perhydroxyl anion is generally believed to be the active bleaching species and its concentration in solution increases with hydrogen peroxide concentration, alkalinity, and temperature (69). The alkaline agents most commonly used to generate HO_2^- are caustic soda, carbonates, silicates, pyrophosphates, and polyphosphates. Better bleaching is obtained at these alkaline conditions by increasing the temperature and by adding stabilizers to prevent the uncontrolled decomposition reactions of hydrogen peroxide. Common stabilizers include silicates, pyrophosphates, and polyaminocarboxylates. These stabilizers may be different from those used to stabilize commercial acidic hydrogen peroxide (70).

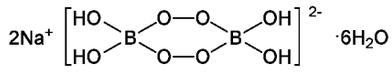
As a bleaching agent, hydrogen peroxide is much less effective than chlorine or hypochlorite; however, it does have several advantages over these bleaching agents. Hydrogen peroxide causes less textile fiber damage, is much gentler on fabric dyes, and does not have a strong odor. Attempts have been made to increase the bleaching power of hydrogen peroxide-based laundry bleaches by the addition of heavy-metal catalysts (71–75). The effectiveness of these systems remains controversial and these catalysts have not been incorporated into commercial products.

Solid Peroxygen Compounds. Hydrogen peroxide reacts with many compounds, such as borates, carbonates, pyrophosphates, sulfates, silicates, and a variety of organic carboxylic acids, esters, and anhydrides to give peroxy compounds or peroxyhydrates. A number of these compounds are stable solids that hydrolyze readily to give hydrogen peroxide in solution.

Perborates. Sodium perborate *[7632-04-4]* is the most widely used solid peroxygen compound. Commercially it is available as a tetrahydrate *[10486-00-7]* and a monohydrate *[10322-33-9]*. The tetrahydrate is produced by treating a borax solution with hydrogen peroxide and sodium hydroxide:

$$Na_2B_4O_7 + 2\,NaOH + 4\,H_2O_2 + 11\,H_2O \rightarrow 4\,NaBO_3{\cdot}4\,H_2O \qquad (16)$$

The tetrahydrate has the structure (8) (76):



(8)

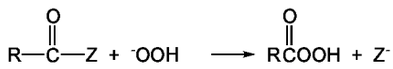
It has good stability and can be used in formulations with many compounds without serious loss of active oxygen. The monohydrate is made by dehydration of the tetrahydrate. The active oxygen contents of the tetrahydrate and monohydrate are 10.5% and 16.0%, respectively. The tetrahydrate is the perborate salt most commonly used in bleaching applications (77). However, as consumer trends move toward more concentrated products, monohydrate is growing in demand because of its higher AO content (78). Because sodium perborate has much greater stability than sodium hypochlorite, it can be formulated into a wide variety of products, including detergents. In the United States, perborates are used in all-fabric bleach formulations, detergents, denture cleaners, tooth powders, and other special cleaners. Sodium perborate is used extensively in Europe in detergent formulations.

Sodium Carbonate Peroxyhydrate. Sodium carbonate peroxyhydrate *[15630-89-4]*, which contains about 14 wt % of active oxygen, has the composition $2Na_2CO_3{\cdot}3H_2O_2$. A white, free-flowing solid, it generally can be used in all applications where perborate is used. Despite the fact that sodium carbonate peroxyhydrate has a greater rate of dissolution than sodium perborate tetrahydrate, the latter is usually favored for its good storage stability and better compatibility with the various materials used in formulations (79).

Peroxymonosulfate. Peroxymonosulfuric acid (Caro's Acid) *[7722-86-3]*, the peroxygen product of hydrogen peroxide and sulfuric acid, is a powerful oxidizing agent; however, because of its instability, it is hazardous (80). It is commercially available in Europe but not in the United States. The salt, potassium permonosulfate *[25482-78-4]* is commercially available under the trade name Oxone. This monopersulfate compound is a white solid having a satisfactory shelf life and an active oxygen content of about 4.5%. It is a triple salt with the composition $2KHSO_5{\cdot}K_2SO_4{\cdot}KHSO_4$. Oxone is used as a bleaching agent and in several other applications where a solid peroxygen source is required; however, the extent of its use is limited.

Peracids. Peracids are compounds containing the functional group —OOH derived from an organic or inorganic acid functionality. Typical structures include $CH_3C(O)OOH$ derived from acetic acid and $HOS(O)_2OOH$ (peroxymonosulfuric acid) derived from sulfuric acid. Peracids have superior cold water bleaching capability versus hydrogen peroxide because of the greater electrophilicity of the peracid peroxygen moiety (81–83). Lower wash temperatures and phosphate reductions or bans in detergent systems account for the recent utilization and vast literature of peracids in textile bleaching (84,85).

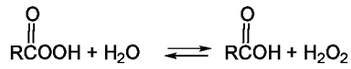
Peracids can be introduced into the bleaching system by two methods. They can be manufactured separately and delivered to the bleaching bath with the other components or as a separate product. Peracids can also be formed *in situ* utilizing the perhydrolysis reaction shown in equation 17.



(17)

R can be a variety of structures. Z is a leaving group and typically the conjugate base of a weak acid whose pK_a can range from 5 to 20 (86). The hydrogen peroxide is typically incorporated into the bath by adding a solid source of peroxide such as sodium percarbonate or the mono- or tetrahydrate of sodium perborate (86).

Peracid Analysis. Peracid concentrations can be measured in a product or in the bath by use of a standard iodide thiosulfate titration (60). With preformed peracids or peracids formed via perhydrolysis care must be exercised to minimize the interference of hydrogen peroxide, present intentionally as a component of the perhydrolysis reaction or as a result of the hydrolysis of the peracid (87,88) as shown in equation 18.



(18)

This is typically accomplished by cooling the titration solution with ice, determining the blank, and titrating rapidly. Another method utilizes determination of the total peroxide and peracid content by use of a ceric sulfate titration to measure hydrogen peroxide followed by a iodide thiosulfate titration to measure total active oxygen (60).

Peracid Classification. Peracids can be broadly classified into organic and inorganic peracids, based on standard nomenclature. The limited number of inorganic peracids has required no subclassification scheme (4). However, the tremendous number of new organic peracids developed (85) has resulted in proposals for classification. For example, a classification scheme based on liquid chromatography retention times and critical micellization constants (CMC) of the parent acids has been proposed (89). The parent acids are used because of the instability of the peracids under chromatographic and micellization measurement conditions. This classification scheme is shown in Table 1.

Table 1. Classification of Peracids

Peracid type	Retention time[a] of parent acid	CMC	Typical structures
hydrophilic	<5 min	>0.5 *M*	peracetic, perpropionic, perbenzoic acids[b]
hydrophobic (surface active)	na	<0.5 *M*	[c]
hydrotropic	>5 min	none, or >0.5 *M*	[c]

[a] Chromatographic conditions: elution with 50:50 methanol water solvent at the rate of 1.5 mL min through a DuPont Zorbax ODS column using a Waters R-401 Refractive Index Detector.

[b] That is, in equations 17 and 18 R CH_3, CH_2CH_3, or C_6H_5, respectively.

[c] See Figure 2.

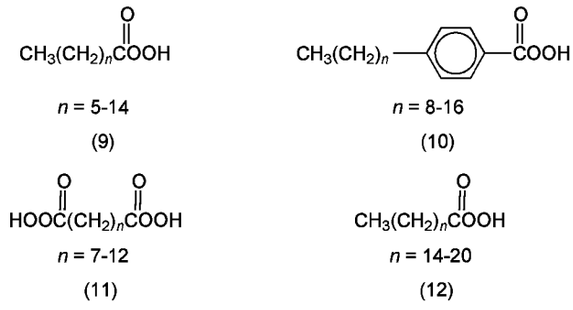
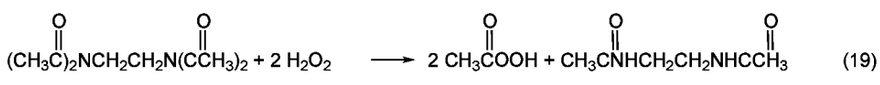


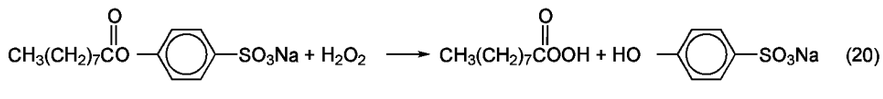
Fig. 2. Typical peracids; see Table 1. Compounds (**9**) and (**10**) are hydrophobic; (**11**) and (**12**) are hydrotropic.

The technique used to classify the peracids is artificial with respect to bleaching, but the classification of a peracid does relate to its location in the bleaching bath microenvironment. Hydrophilic peracids are quite water-soluble and as such they are located in the bulk phase and their bleaching performance is the result of random collisions with the fabric surface (4). Since collisional frequency is increased at higher temperature the hydrophilic peracids are useful in high temperature washing conditions. The inorganic peracids are exclusively of the hydrophilic type. Hydrophobic peracids are similar in structure and behavior to common detergent surfactants because they possess a hydrophilic head group (—C(O)OOH) and a hydrophobic tail ($CH_3(CH_2)_n$—). These peracids have a defined CMC and as such are likely to be located in micelles (4,90). The ability of these peracids to partition to an interface make them more suitable for cold water washing than hydrophilic peracids (91,92). At cooler temperatures improved stain removal by the hydrophobic bleaches versus the hydrophilic bleaches has been demonstrated. No reports of the hydrotropic peracid bleach microenvironment locale have been published, but because of their oily character and based on Table 1 they are likely dissolved into the detergent micelle.

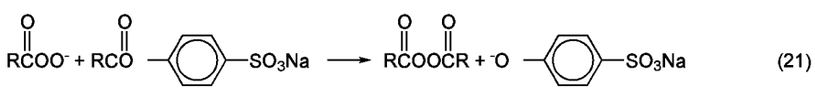
Peracid Precursor Systems. Compounds that can form peracids by perhydrolysis are almost exclusively amide, imides, esters, or anhydrides (85). Two compounds were commercially used for laundry bleaching as of 1990. Tetraacetylethylenediamine (TAED) *[10543-57-4]* is utilized in over 50% of Western European detergents (5). The perhydrolysis reaction of this compound is shown in equation 19. TAED generates two moles of peracid and one mole of diacetylethylenediamine per mole of imide (93).



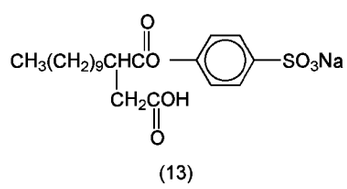
The perhydrolysis reaction could theoretically continue to give four moles of peracid per mole of TAED but stops at this stoichiometry because of the substantial increase in the conjugate acid pK_a of the leaving group going from an amide (pK_a 17) to an amine (pK_a 35) (94,95). Nonanoyloxybenzene sulfonate (NOBS) *[101482-85-3]* is used in detergent products in the United States and Japan. The NOBS perhydrolysis reaction is shown in equation 20 (96).



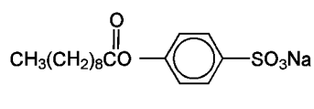
The NOBS system undergoes an additional reaction that forms a diacyl peroxide as a result of the nucleophilic attack of the peracid anion on the NOBS precursor as shown in equation 21. This undesirable side reaction can be minimized by the use of an excess molar quantity of hydrogen peroxide (91,96) or by the use of shorter dialkyl chain acid derivatives. However, the use of these acid derivatives also appears to result in less efficient bleaching. The dependence of the acid group on the side product formation is apparently the result of the proximity of the newly formed peracid to unreacted NOBS in the micellar environment (91). A variety of other peracid precursor structures can be found (97–118).



The pK_a of the leaving group and the hydrophobe chain length can dramatically affect the efficiency of the perhydrolysis reaction. Additionally, the structure of the acid portion of the precursor can affect the yield and sensitivity of the reaction to pH. The mono-4-hydroxybenzenesulfonic acid ester of α-decylsuccinic acid (13) undergoes extremely efficient perhydrolysis at much lower pHs than other peracid precursors, eg, decanoyloxybenzene sulfonate (14). This may be because of the neighboring group participation of the adjacent carboxylate as shown in Table 2 (115).



(13)



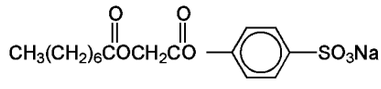
(14)

Table 2. Effect of Alpha-Carbonyl Group on Peracid Yield

Compound	Molecular formula[a]	pH	Peracid yield
(**13**)	$C_{20}H_{30}O_7S$	9.5	97%
(**14**)	$C_{1}H_{24}O_5S$	9.5	26%

[a] Of the sulfonic acid.

Electronic effects within the acid portion of the precursor have also been utilized for enhanced reactivity. The 4-hydroxybenzenesulfonate ester of octanoyloxyacetic acid, (15), undergoes efficient perhydrolysis at lower pHs because of the activation of the susceptible carbonyl by the beta-oxygen of the hydrophobic tail (100).

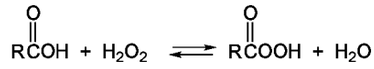


(15)

Attempts have also been made to reduce the odor associated with the peracid in the home laundry. Use of a precursor that generates the peracid of a fatty acid can result in an objectionable odor in the wash bath (106). This odor is exacerbated by the higher pK_a of the peracid versus its parent acid resulting in a greater proportion of the peracid in the unionized and therefore less water-soluble form. To mitigate this circumstance, functionalization of the fatty tail typically alpha to the carbonyl has been utilized (112). The modifications include alpha-chloro and alpha-methoxy substituents on the parent acid portion of the precursor ester.

The peracid precursors can be susceptible to hydrolysis or perhydrolysis in the solid state particularly when incorporated into a detergent product that is exposed to high humidity conditions (118). To minimize the loss of precursor over time the material can be incorporated into granules to minimize the surface area to volume ratio, which minimizes storage instability. A variety of granulation techniques have been described in the literature of which extrusion and agglomeration have been commercialized (119–131). A limited number of references also discuss the incorporation of a precursor into a liquid matrix that contains either hydrogen peroxide or an insoluble source of hydrogen peroxide such as perborate (132,133).

Preformed Peracids. Peracids can be generated at a manufacturing site and directly incorporated into formulations without the need for *in situ* generation. Two primary methods are utilized for peracid manufacture. The first method uses the equilibrium shown in equation 22 to generate the peracid from the parent acid.



(22)

The equilibrium is shifted by removal of the water (134) or removal of the peracid by precipitation (135,136). Peracids can also be generated by treatment of an anhydride with hydrogen peroxide to generate the peracid and a carboxylic acid.

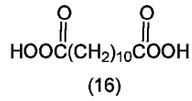
(23)

The latter method typically requires less severe conditions than the former because of the labile nature of the organic anhydride (87,137). Both of these reactions can result in explosions and significant precautions should be taken prior to any attempted synthesis of a peracid (87). For solid peracids the reaction mixture can be neutralized with sodium hydroxide and the resulting filtercake washed with water. In the case of the sulfuric acid mediated reaction the peracid has sodium sulfate incorporated in the cake (135). The water of hydration present in the sodium sulfate is desirable to prevent detonation or deflagration of the solid peracid when isolated in a dry state (87,138,139).

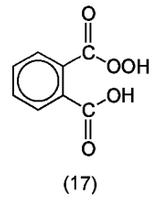
The water of hydration, particularly that incorporated in sodium sulfate decahydrate, however, can cause instability when the peracid–sulfate blend is subjected to elevated temperatures. To mitigate this problem materials known as exotherm control agents have been incorporated into peracid formulas. These materials release their water only when conditions occur that could lead to detonation or deflagration. Magnesium sulfate heptahydrate, magnesium sulfate–sodium sulfate tetrahydrate, and boric acid each release water near 100°C (138,140). The release of the water prevents the propagation of the decomposition of the peracid by removing heat via evaporation (140). These materials are incorporated into the peracid composition at concentrations up to equal weight by weight to the peracid.

The peracid–exotherm control agent mixtures can be granulated using a variety of techniques common in the industry, including agglomeration. As with peracid precursors, the surface area to volume ratio can impact the stability of the peracid. Particles are thus made as large as possible to maintain stability (141).

Two solid organic peracids have been utilized in textile bleaching products. Diperoxydodecanedioic acid, (16), *[66280-55-5]*, a hydrotropic peracid, and the magnesium salt *[78948-87-5]* of monoperoxyphthalic acid, (17), *[2311-91-3]*, a hydrophilic peracid, were contained in bleaching products for a short period of time (142).



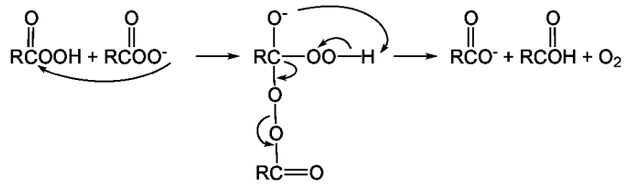
(16)



(17)

Peracids are also available as aqueous solutions that contain the peracid in equilibrium with hydrogen peroxide and the parent acid. Peracetic acid *[79-21-0]* is commercially available as a 40% solution in dilute acetic acid. The water and dilution of the peracid make these solutions easier to handle than their solid counterparts, but they still require careful handling and protection from heat.

Peracid Decomposition. Peracids, whether preformed or formed *in situ* via the perhydrolysis reaction, are susceptible to decomposition in an aqueous bleaching bath. The decomposition is caused by the occurrence of one of four reactions. The peracid can decompose as a result of oxidation of the bleachable material. Transition metals present even at extremely low concentration in the bath from the incoming water can decompose the peracid catalytically (143,144). To minimize this effect, metal-sequestering agents have been proposed to prevent the degradation of the peracid in solution (143,144). Peracids can also hydrolyze to the parent acid and hydrogen peroxide because of the large excess of water present in the aqueous bleaching bath. This is generally a kinetically slow process (87). A final decomposition mechanism involves the reaction of two moles of peracid generating two moles of parent acid and a mole of oxygen.



The reaction involves the nucleophilic attack of a peracid anion on the unionized peracid giving a tetrahedral diperoxy intermediate that then eliminates oxygen giving the parent acids. The observed rate of the reaction depends on the initial concentration of the peracid as expected in a second-order process. The reaction also depends on the structure of the peracid (specifically whether the peracid can micellize) (4). Micellization increases the effective second-order concentration of the peracid because of the proximity of one peracid to another. This effect can be mitigated by the addition of an appropriate surfactant, which when incorporated into the peracid micelle, effectively dilutes the peracid, reducing the rate of decomposition (4,90).

REDUCING BLEACHES

The reducing agents generally used in bleaching include sulfur dioxide, sulfurous acid, bisulfites, sulfites, hydrosulfites (dithionites), sodium sulfoxylate formaldehyde, and sodium borohydride. These materials are used mainly in pulp and textile bleaching (see SULFUR COMPOUNDS; BORON COMPOUNDS).

Sulfur Dioxide, Sulfites, and Bisulfites. Sulfur dioxide *[7446-09-5]* and its derivatives have been used to bleach textiles since earliest times. Sulfur dioxide is a gas formed by burning sulfur in air. Besides being an important bleaching agent in the pulp and paper industry, sulfur dioxide is also integral to some processes for chlorine dioxide, sodium hydrosulfite, and sodium sulfite. Sulfur dioxide is used in both Kraft and mechanical pulp processes, and it is unique in that its bleaching effect is independent of pH over the range 3–10 (145). When SO_2 is dissolved in water, it yields a complex mixture given the trivial name sulfurous acid *[7782-99-2]* (H_2SO_3), which contains SO_2, H_3O^+, $S_2O_5^{2-}$, and HSO_3^-. The composition of the mixture depends on the concentration of the sulfur dioxide in the water, the pH, and the temperature (146). Although sulfurous acid does not exist in the free state, it forms stable salts (the neutral sulfite, SO_3^{2-}, and the hydrogen sulfite or bisulfite HSO_3^-) which are good reducing agents (eqs. 25, 26).

$$2\,SO_3^{2-} + O_2 \rightarrow 2\,SO_4^{2-} \tag{25}$$

$$HSO_3^- + Cl_2 + 2\,OH^- \rightarrow HSO_4^- + 2\,Cl^- + H_2O \tag{26}$$

Sodium sulfite *[7757-83-7]*, which is used in pulp and paper bleaching, is usually produced by the reaction of sulfur dioxide with either caustic soda or soda ash.

$$SO_2 + 2\,NaOH \rightarrow Na_2SO_3 + H_2O \tag{27}$$

$$SO_2 + Na_2CO_3 \rightarrow Na_2SO_3 + CO_2 \tag{28}$$

Dithionites. Although the free-dithionous acid, $H_2S_2O_4$, has never been isolated, the salts of the acid, in particular zinc *[7779-86-4]* and sodium dithionite *[7775-14-6]* have been prepared and are widely used as industrial reducing agents. The dithionite salts can be prepared by the reaction of sodium formate with sodium hydroxide and sulfur dioxide or by the reduction of sulfites, bisulfites, and sulfur dioxide with metallic substances such as zinc, iron, or zinc or sodium amalgams, or by electrolytic reduction (147).

$$2\,HSO_3^- + SO_2 + Zn \rightarrow ZnSO_3\downarrow + S_2O_4^{2-} + H_2O \tag{29}$$

Aqueous solutions of dithionite are not stable in the presence of oxygen, low pH, or elevated temperatures. The decomposition of dithionite occurs by the following equation:

$$2\,S_2O_4^{2-} + H_2O \rightarrow 2\,HSO_3^- + S_2O_3^{2-} \tag{30}$$

Both sodium dithionite and zinc dithionite are produced commercially, though the uses of this latter salt have declined because of the regulatory constraints on pollution of water by zinc. The zinc salt is used under those conditions of pH and temperature where the sodium dithionite would be unstable. The principal applications of these compounds are in bleaching of mechanical pulp and in dyeing, printing, and stripping in the textile industry. A derivative of sodium dithionite is sodium sulfoxylate formaldehyde, which is prepared by the reaction of formaldehyde with the dithionite. Its applications are like those of dithionite except that it is less reactive and more stable thermally. When the sulfoxylate is used, a pH range of 3.2–3.5 produces the best results. For both the dithionite salts and sulfoxylate, the higher the temperature, the greater the reducing strength. The sulfoxylates can be used at temperatures as high as 100°C.

The principal bleaching applications of sodium dithionite are in the bleaching of mechanical or CTM pulps and the bleaching of kaolin clays for use as filler for fine paper. Other applications include the bleaching of glues, gelatin, soap, and food products. A significant new application for dithionite is in the bleaching of recycled paper.

The Mechanism of Bleaching

Bleaching is a decolorization or whitening process that can occur in solution or on a surface. The color-producing materials in solution or on fibers are typically organic compounds that possess extended conjugated chains of alternating single and double bonds and often include heteroatoms, carbonyl, and phenyl rings in the conjugated system. The portion of molecule that absorbs a photon of light is referred to as the chromophore (Greek: *color bearer*). For a molecule to produce color the conjugated system must result in sufficiently delocalized electrons such that the energy gap between the ground and excited states is small enough so that photons in the visible portion of the light spectrum are absorbed (see COLOR).

Bleaching and decolorization can occur by destroying one or more of the double bonds in the conjugated chain, by cleaving the conjugated chain, or by oxidation of one of the other moieties in the conjugated chain. The result of any one of the three reactions is an increase in the energy gap between the

ground and excited states, so that the molecule then absorbs light in the ultraviolet region, and no color is produced. Bleaching may also increase the water solubility of organic compounds after reaction. Conversion of an olefin to a vicinal diol, for example, dramatically increases the polarity and consequently water solubility of the compound. A variety of bleaching agents can affect this transformation. The increased solubility allows actual removal of the bleached substance from a surface.

Chlorine bleaches react with more chromophores than oxygen bleaches. They react irreversibly with aldehydes, alcohols, ketones, carbon–carbon double bonds, acidic carbon–hydrogen bonds, nitrogen compounds, sulfur compounds, and aromatic compounds. Mixtures of products are usually formed because of the variety of active forms in equilibrium with each other (11). Also, many reactions occur in a series of steps, of which the first is usually rate-limiting. With hypochlorous acid, the first step often involves electrophilic addition to carbon–carbon double bonds to form chlorohydrins and epoxides. Or, it may involve electrophilic substitution of aromatic or acidic hydrogens by chlorine. Free-radical reactions are also possible. Nucleophilic addition also occurs with hypochlorite anion, which forms oxygenated products via the elimination of HCl. Aliphatic compounds usually react further to form acids, carbon dioxide, and ketones. Also, most carbon–carbon double bonds and carbon–carbon bonds with adjacent carbonyl or hydroxyl groups can be cleaved. Similar results are often obtained with chlorine dioxide. However, chlorine dioxide reacts with slightly fewer functional groups and often at slower rates than chlorine or hypochlorous acid. Chlorine dioxide also reacts by different mechanisms, which are generally less well understood. With some substrates the main products are chlorinated, but the percentage is usually less than with chlorine or hypochlorous acid (57,148,149).

The mechanism of bleaching of hydrogen peroxide is not well understood. It is generally believed that the perhydroxyl anion (HOO ;) is the active bleaching species since both the concentration of this anion and the rate of the bleaching process increase with increasing pH (70). Whereas the role of free-radical reactions in the bleaching process remains speculative, mechanisms involving heavy-metal catalyzed reactions are generally undesirable, since they often reduce the effective bleaching because of the rapid loss of peroxide and may also result in fabric damage if the metal is entrapped in the fabric (150). Hydrogen peroxide and other peroxygen compounds can destroy double bonds by epoxidation. This involves addition of an oxygen atom across the double bond usually followed by hydrolysis of the epoxide formed to 1,2-diols under bleaching conditions.

Peracids undergo a variety of reactions which result in bleaching. Peracids can add an oxygen across a double bond to give an epoxide, which can undergo further reactions including hydrolysis to give a vicinal diol. Peracids can oxidize aldehydes to acids, sulfur compounds to sulfoxides and sulfones, and nitrogen compounds to amine oxides, hydroxylamines, and nitro compounds (85). Peracids can also oxidize alpha-diketone compounds to anhydrides and ketones to esters. The protonated and deprotonated forms of the peracids are both effective bleaches. The protonated form acts as an electrophile whereas the deprotonated form is a nucleophilic oxidant.

Reducing agents are thought to work by reduction of the chromophoric carbonyl groups in textiles or pulp.

Applications of Bleaching Compounds

Laundering and Cleaning.

Home and Institutional Laundering. The most widely used bleach in the United States is liquid chlorine bleach, an alkaline aqueous solution of sodium hypochlorite. This bleach is highly effective at whitening fabrics and also provides germicidal activity at usage concentrations. Liquid chlorine bleach is sold as a 5.25% solution and 1 cup provides 200 ppm of available chlorine in the wash. Liquid chlorine bleaches are not suitable for use on all fabrics. Dry and liquid bleaches that deliver hydrogen peroxide to the wash are used to enhance cleaning on fabrics. They are less efficacious than chlorine bleaches but are safe to use on more fabrics. The dry bleaches typically contain sodium perborate in an alkaline base whereas the liquid peroxide bleaches contain hydrogen peroxide in an acidic solution. Detergents containing sodium perborate tetrahydrate are also available.

The worldwide decreasing wash temperatures, which decrease the effectiveness of hydrogen peroxide based bleaches, have stimulated research to identify activators to improve bleaching effectiveness. Tetraacetylethylenediamine is widely used in European detergents to compensate for the trend to use lower wash temperatures. TAED generates peracetic acid in the wash in combination with hydrogen peroxide. TAED has not been utilized in the United States where one activator nonanoyloxybenzene sulfonate (NOBS) has been commercialized and incorporated into several detergent products. NOBS produces pernonanoic acid when combined with hydrogen peroxide in the washwater and is claimed to provide superior cleaning to perborate bleaches.

In industrial and institutional bleaching either liquid or dry chlorine bleaches are used because of their effectiveness, low cost, and germicidal properties. Dry chlorine bleaches, particularly formulated chloroisocyanurates, are used in institutional laundries.

Hard Surface Cleaners and Cleansers. Bleaching agents are used in hard surface cleaners to remove stains caused by mildew, foods, etc, and to disinfect surfaces. Disinfection is especially important for many industrial uses. Alkaline solutions of 1–5% sodium hypochlorite that may contain surfactants and other auxiliaries are most often used for these purposes. These are sometimes thickened to increase contact times with vertical surfaces. A thick, alkaline cleaner with 5% hydrogen peroxide is also sold in Europe. Liquid abrasive cleansers with suspended solid abrasives are also available and contain about 1% sodium hypochlorite. Powdered cleansers often contain 0.1–1% available chlorine and they may contain abrasives. Sodium dichloroisocyanurate is the most common bleach used in powdered cleansers, having largely replaced chlorinated trisodium phosphate. Calcium hypochlorite is also used. Dichloroisocyanurates are also used in effervescent tablets that dissolve quickly to make cleaning solutions. In-tank toilet cleaners use calcium hypochlorite, dichloroisocyanurates, or *N*-chlorosuccinimide to release hypochlorite with each flush to prevent stains from forming. One powdered toilet bowl cleaner uses potassium peroxymonosulfate and sodium chloride to generate hypochlorite in *in situ*.

Automatic Dishwashing and Warewashing. The primary role of bleach in automatic dishwashing and warewashing is to reduce spotting and filming by breaking down and removing the last traces of adsorbed soils. They also remove various food stains such as tea. All automatic dishwashing and warewashing detergents contain alkaline metal salts or hydroxides. Liquids, gels, and slurries contain 1–3% sodium hypochlorite. Powders and tablets almost always use 1–4% sodium dichloroisocyanurate dihydrate. Trichloroisocyanurate and the once popular chlorinated trisodium phosphate are also used. A few powders use sodium percarbonate or sodium perborate. They are less effective than chlorine bleaches, but this is largely overcome by increased amounts of alkaline metal salts or hydroxides. Enzymes (qv) also work with peroxygen bleaches but are deactivated by chlorine bleaches. Sodium hypochlorite or chloramine T are also used as sanitizers in the last rinse of low temperature warewashing.

Textile Bleaching. Many textiles are bleached to remove any remaining soil and colored compounds before dyeing and finishing (see TEXTILES). Bleaching is usually preceded by washing in hot alkali to remove most of the impurities in a process called scouring. Bleaching is usually done as part of a continuous process, but batch processes are still used. Not all fabrics are bleached, but natural fibers and their blends usually are. To minimize fiber damage, a minimum of bleaching agent is used. Making white and lightly colored fabrics requires the most bleaching. Bleaching conditions vary widely, depending on the equipment, the bleaching agent, the type of fiber, and the amount of whiteness required for the end use (58,59,151–154).

Cotton and Cotton–Polyester. Cotton is the principal fiber bleached today, and almost all cotton is bleached. About 80–90% of all cotton and cotton–polyester fabric is bleached with hydrogen peroxide. With hydrogen peroxide the fabric does not need to be scoured before bleaching and there is little risk of overbleaching. Typically, bleaching with 0.3–0.6% hydrogen peroxide solutions at pH 10.5–11.5 is done for 1–3 h at 90–95°C. The time can be reduced to 2–15 min by increasing the severity of the scouring step, impregnating the fabric with larger amounts of hydrogen peroxide, and using steam to attain temperatures of 95–100°C. In pressurized vessels at 130–145°C the time is reduced to 0.75–2 min. In order to save energy, some plants combine scouring and bleaching with hydrogen peroxide into a single step. Other plants use cold bleaching in which the textiles are scoured, bleached with sodium hypochlorite, and then bleached with hydrogen peroxide at room temperature for 4–5 h with a catalyst (155), or for 12–16 h without a catalyst. With all processes, bleaching with hypochlorite or chlorine dioxide may precede peroxide bleaching when white or lightly colored textiles are desired.

In the past, sodium hypochlorite solution (called chemic by textile workers) was the most commonly used bleach. Some is still used today because of its lower cost and better whitening ability than hydrogen peroxide. However, bleaching with hypochlorite needs to be carefully controlled to prevent fiber damage. Also, when only hypochlorite bleach is used, the fabrics need to be well scoured first to remove soils that consume hypochlorite. Otherwise higher hypochlorite concentrations and longer bleaching times are needed, which increase the risk of fabric damage. Protein soils may also form chloramines that cause color reversion. Solutions of 0.1–0.5% sodium hypochlorite are typically used at pH 10–11.5 for 0.5–4 h at 20°C or for 15–30 min at 40–50°C. The fabric is then bleached with hydrogen peroxide, or it is washed in a solution of a reducing agent (antichlor), such as bisulfite or sulfur dioxide, to remove residual hypochlorite and chloramines.

Sodium chlorite is also used to bleach some cotton and cotton–polyester fabrics. Unlike peroxide and hypochlorite, which only whiten the cotton portion of cotton–polyester blends, sodium chlorite also whitens polyester. However, the polyester portion usually does not need to be whitened. Sodium chlorite whitens better than hydrogen peroxide, does not damage fibers, and can be used with unscoured fabrics. However, it is more expensive, more corrosive to metals, and more hazardous than peroxide or hypochlorite. Typically, solutions of 0.1–3% sodium chlorite with sufficient dihydrogen phosphate and formic acid to give pH 3.8–4.2 are used at 80–95°C for 1–6 h. In a room temperature process, fabric is treated overnight with a neutral solution of sodium chlorite that is activated by formaldehyde. Minor bleaching agents that are used in a manner similar to hydrogen peroxide are sodium peroxide *[1313-60-6]*, sodium perborate, and sodium percarbonate *[20745-24-8]*. Perborate or percarbonate are most frequently used as additives to scouring solutions in place of a separate bleaching step when a fully whitened fabric is not needed.

Other Cellulosics. Rayon is bleached similarly to cotton but under milder conditions since the fibers are more easily damaged and since there is less colored material to bleach. Cellulose acetate and triacetate are not usually bleached. They can be bleached like rayon, except a slightly lower pH is used to prevent hydrolysis. The above fibers are most commonly bleached with hydrogen peroxide. Linen, flax, and jute require more bleaching and milder conditions than cotton, so multiple steps are usually used. Commonly an acidic or neutral hypochlorite solution is followed by alkaline hypochlorite, peroxide, chlorite, or permanganate, or a chlorite step is done between two peroxide steps. A one-step process with sodium chlorite and hydrogen peroxide is also used.

Synthetic Fibers. Most synthetic fibers are sufficiently white and do not require bleaching. For white fabrics, unbleached synthetic fibers with fluorescent whitening agents are usually used. When needed, synthetic fibers and many of their blends are bleached with sodium chlorite solutions at pH 2.5–4.5 for 30–90 min at concentrations and temperatures that depend on the type of fiber. Solutions of 0.1% peracetic acid are also used at pH 6–7 for 1 h at 80–85°C to bleach nylon.

Wool and Silk. Wool must be carefully bleached to avoid fiber damage. It is usually bleached with 1–5% hydrogen peroxide solutions at pH 8–9 for several hours at 40–55°C or at pH 5.5–8 for 20–60 min at 70–80°C. Silk is bleached similarly, but at slightly higher temperatures.

Wool with dark pigmented fibers is treated with ferrous sulfate, sodium dithionite, and formaldehyde before it is bleached with hydrogen peroxide. The ferrous ions are absorbed by the dark pigments where they increase the bleaching done by the peroxide.

Wool may also be bleached with reducing agents, usually after bleaching with hydrogen peroxide. This is the normal practice with wool blends. In the reducing step, 0.2–0.5% sodium dithionite solutions are often used at pH 5.5–7 for 1–2 h at 45–65°C. Faster bleaching is obtained with zinc hydroxymethane-sulfinate *[24887-06-7]* below pH 3 and above 80°C.

The ancient process of stoving is still occasionally used to bleach wool and silk with sulfur dioxide. In this process, wet fabrics are hung in chambers of burning sulfur or sulfur dioxide gas for at least 8 h. The fabrics are then washed with sodium sulfite to remove excess sulfur dioxide. Fabric so treated may have unpleasant odors, and the original color eventually returns, but the process is simple and inexpensive.

Bleaching of Other Materials.

Hair. Hydrogen peroxide is the most satisfactory bleaching agent for human hair. Solutions containing 3–4% hydrogen peroxide, available from drug stores and supermarkets, are commonly used. In beauty shops, more rapid bleaching is desired and a 5–6% solution is used. Ammonium hydroxide is usually the source of alkalinity in both systems (see COSMETICS; HAIR PREPARATIONS).

Fur. Fur is bleached to permit dyeing to the desired shade. The coloring matter in fur is usually bleached using hydrogen peroxide stabilized with sodium silicate. For difficult to bleach dark hairs it is necessary to add a step using a reducing agent with a catalyst such as ferrous sulfate. The formula and procedures are the same as those used for wool.

Foodstuffs, Oils. Sulfur dioxide is used to preserve grapes, wine (qv), and apples; the process also results in a lighter color. During the refining of sugar (qv), sulfur dioxide is added to remove the last traces of color. Flour can be bleached with a variety of chemicals including chlorine, chlorine dioxide, oxides of nitrogen, and benzoyl peroxide *[94-36-0]*. Bleaching agents such as chlorine dioxide or sodium dichromate *[10588-01-9]* are used in the processing of nonedible fats and fatty oils for the oxidation of pigments to colorless forms (see FOOD PROCESSING).

Economic Aspects

The chemicals used for bleaching have a variety of uses outside of bleaching technology. As a consequence, detailed information regarding production of these materials for bleach use is limited.

Industry sources indicate worldwide production of hydrogen peroxide and sodium perborate mono- and tetrahydrate, which are used almost exclusively for bleach applications, is 1.1×10^6 t per year and 6.4×10^5 t per year, respectively, in 1990.

A study of the North American bleaching agent market was completed in June 1988 and includes consumption quantities for the year 1986 (156). Chlorine consumption for 1986 was 1.86×10^6 t. The North American consumption volume of other chlorine-containing bleaching compounds including sodium and calcium hypochlorite, chlorinated isocyanurates, and hydantoins was 286,000 t. The 1986 North American consumption of sodium chlorate was estimated at 5.5×10^5 t.

Tetraacetylethylenediamine (TAED) perborate activator production has been estimated by industry sources to be 54,000 t to 63,600 t per year as of 1990. The production is located solely in Western Europe where the product is consumed. No estimates of the perborate activator nonanoyloxybenzene sulfonate production volumes are available because it is captive chemical of the Procter & Gamble Co.

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PULP AND PAPER

Worldwide, more than 50 million tons of pulp is bleached annually, making the pulp and paper industry one of the largest consumers of bleaching chemicals. Most of the pulp bleached is made by separating wood into its component fibers, either chemically or mechanically. Mechanical pulp is made either by forcing wood chips through a narrow gap between rotating disks in so-called refiners or by stone grinding of logs. Its chemical composition closely parallels that of the original wood, the primary components being cellulose, other polysaccharides or hemicelluloses, lignin, and minor amounts of solvent-extractable materials. Chemical pulp is made by cooking the wood in an aqueous solution of chemicals that are able to break down and dissolve lignin, allowing the fibers to separate. The dominant kraft or sulfate process uses an alkaline sulfide solution and produces pulp that is both stronger and darker colored than sulfite pulps made with acidic liquor. Compared to mechanical pulp, chemical pulp is stronger, more permanent, and capable of being bleached to higher brightness. It is therefore used in products requiring one or more of these qualities, whereas the less costly mechanical pulp is used in newsprint and other short-lived printing papers that do not require high brightness and high strength. A third broad class of pulp types is made in processes that rely on various combinations of chemical and mechanical methods. Semichemical and chemimechanical pulps, for example, are made by disk refining of chips after a mild chemical treatment.

The principal objective in bleaching any type of pulp is usually to increase the whiteness of the pulp, as measured by its brightness, which is defined as reflectance measured at a wavelength of 457 nm. Depending on end use, however, other criteria may rival brightness in importance. These include cleanliness, or freedom from particles of bark and unpulped wood, resistance to yellowing upon light irradiation or storage, and removal of hemicellulose and extractives.

Chemical Pulp

Virtually all of the color of any pulp resides in its lignin *[9005-53-2]* component. It is not possible to remove all of the lignin from the wood during pulping because concurrent cellulose damage would seriously weaken the fibers. Pulping is therefore terminated when 5–8% of the original lignin remains. Bleaching may therefore be regarded as a more selective continuation of the pulping process, but there are important distinctions to be made between these two phases of delignification. Side reactions during pulping cause the residual lignin to be both darker in color and more tightly bound to the fiber than native lignin. From a practical point of view, a more important distinction concerns the fate of the organic material removed. Spent pulping liquors are recycled to a chemical recovery system, where they are concentrated and burned to generate energy. Bleaching effluent, on the other hand, is typically contaminated with chloride ion and chlorine compounds, making it difficult or impossible to recycle it to the recovery system because of potential for corrosion. It is therefore necessary to treat and discharge the bleaching effluent. Associated environmental concerns are presently causing rapid changes in bleaching technology.

Bleaching Sequences. The application of increasing amounts of any bleaching chemical results in progressively smaller brightness increases per unit weight of chemical added. Because the asymptotic limit is usually far below the final brightness target, and because it is approached only at high chemical charges, single-stage bleaching is both ineffective and uneconomical. As a result, chemical pulps are invariably bleached in multistage processes, usually with washing between stages to limit chemical consumption. A shorthand notation for bleaching sequences uses single capital letters to designate individual bleaching agents, as follows: C — chlorine, E — caustic extraction, D — chlorine dioxide, O — oxygen, P — hydrogen peroxide, H — hypochlorite, and Z — ozone. Stages employing only one chemical are designated by a single letter, those using combinations by a variety of notations, such as C_D, D/C, (C + D), etc. Sequences of from three to six stages are common. The first two or three usually remove the bulk of the residual lignin and, depending on the exact nature of the sequence, may not increase the brightness significantly. These stages comprise the delignifying partial sequence. Examples are CE, (CD)E, and O(CD)E, the last being an example of a partial sequence where delignification is accompanied by some brightening. The final one to four stages accomplish a large brightness increase with little lignin removal and comprise the brightening partial sequence. Examples are D, DP, DED, and D(EP)D.

Desirable Attributes of Bleaching Agents. An ideal bleaching agent for chemical pulp would have high selectivity, reactivity, efficiency, and particle bleaching ability, while simultaneously having low equivalent weight and low potential for harm to the environment. With the exception of caustic, all important chemical pulp bleaching agents are oxidants. Low equivalent weight is desirable because it translates to a small chemical requirement for the transfer of a given number of electrons. Efficiency refers to the degree to which these electrons are transferred in productive processes, such as lignin depolymerization and chromophore destruction, as opposed to unproductive ones such as decomposition and soluble product fragmentation.

Chlorine. Chlorine *[7782-50-5]*, Cl_2, is used either in the first stage of the sequence or in the stage immediately following an oxygen predelignification stage. Its chief function is to render most of the residual lignin soluble in alkali, and it is always followed by a caustic extraction stage. The mechanisms by which solubilization occurs include demethylation, alkyl–aryl ether cleavage, aromatic substitution, and oxidation (1). An important variable is pH, which is kept below 2 to avoid excessive hydrolysis of chlorine to hypochlorous acid *[7790-92-3]*, HOCl, which can attack cellulose. A salient feature of chlorination is its extreme rapidity. In a perfectly mixed system, the bulk of the reaction is complete within seconds and a subsequent slower phase is virtually complete within a few additional minutes (2). This, together with the extreme slowness of diffusion of chlorine in pulp suspensions, makes good mixing very important (3). Accordingly, traditional chlorination stages were conducted at low pulp consistency (3–4% dry fiber on pulp suspension-weight basis), to facilitate good mixing, and at low temperature (5–30°C), to decrease the rate of reaction relative to that of diffusion and to increase selectivity for lignin. Modern chlorination stages are run at either low or medium (10–12%) consistency and higher temperature (40–60°C). Medium consistency operation has been made possible by the introduction of high shear, fluidizing mixers. High temperature operation is facilitated by good mixing and also by the selectivity improvement that comes from substituting chlorine dioxide for part of the chlorine used. A retention time of 30–60 min is provided to allow for process upsets and less than perfect mixing. Chlorine is applied at a rate that is proportional to the lignin content, as measured by "kappa number", of the pulp entering the stage. This can vary widely, depending on whether softwood or hardwood is the raw material, whether a preceding oxygen stage is used, and whether new extended delignification technology is used in the pulping step. Chlorine charges of 3–7% have been common, but an environmentally driven downward trend is evident. This has arisen out of concern over possible environmental effects of chlorinated organic by-products. The formation of these by-products is now commonly reduced by substituting chlorine dioxide for part or all of the chlorine used.

Caustic Extraction. A relatively small amount of lignin dissolves during chlorination; most is removed in the subsequent caustic extraction stage. The charge of sodium hydroxide *[1310-73-2]*, NaOH, is proportional to the amount of chlorine in the previous stage and is controlled to maintain exit pH 10.5 or above. Typical conditions are 1–2 h at 60–80°C and 10–12% consistency. Oxygen is very frequently added, either alone or with hydrogen peroxide, to effect more complete lignin removal and to decrease downstream bleaching chemical costs (4). Alternatively, the benefit of oxygen addition may be realized in the form of a reduction in chlorine application to meet environmental demands.

Chlorine Dioxide. Chlorine dioxide *[10049-04-4]*, ClO_2, offers a unique combination of low equivalent weight (13.5 vs 35.5 for chlorine), extremely high selectivity for lignin, high efficiency, ability to bleach to very high brightness, and good particle bleaching ability (5). It is versatile, inasmuch as it can be used both to brighten and to delignify, and in the latter role it interacts synergistically with chlorine. Furthermore, it is less likely than chlorine to have significant environmental impact since it forms a much smaller amount of chlorinated organic by-products for a given bleaching effect.

Although chlorine dioxide is toxic and, when present in sufficiently high concentration, explosive, a variety of processes are available for safe on-site

generation (6). All involve reaction of a reducing agent with sodium chlorate *[7758-9-2]*, $NaClO_3$, in acid medium; significant differences between them include their relative rates of production of chlorine, sodium sulfate *[7757-82-6]*, Na_2SO_4, and acid by-products, all of which can present disposal problems. The reducing agent can be sulfur dioxide *[7446-09-5]*, SO_2, methanol *[67-56-1]*, CH_3OH, or chloride ion.

Chlorine dioxide is widely used in chemical pulp bleaching. Brightening stages are conducted for 2–5 h at 10–12% consistency, 60–80°C and pH 3–5. The chemical charge varies from 0.1–1.2%, depending on the type of pulp, the length of the sequence, and the number of chlorine dioxide stages present. Reactions occur with free phenolic groups and aliphatic double bonds and encompass demethylation and ring cleavage reactions (1). However, chlorine dioxide, unlike chlorine, is relatively unreactive toward fully etherified phenolic units in lignin. It is nearly inert toward cellulose and other carbohydrates in the pulp.

An increasingly important role for chlorine dioxide is as a delignifying agent in the first stage. Small amounts (0.05–0.15%) of chlorine dioxide have been added to chlorination stages for many years, the main objective being to prevent cellulose degradation by chlorine (7). In this application, chlorine dioxide is believed to act as a free-radical scavenger. Substitution of chlorine dioxide for large fractions (50–70%) of the chlorine requirement has also been practiced for a long time, but, until recently, in relatively few instances (7). Growing concern over chlorinated by-products has changed this, and the use of high levels of chlorine dioxide substitution is becoming widespread (8). Furthermore, there is a growing demand for pulp bleached without the use of elemental chlorine, particularly from European markets. To meet this demand, some mills operate for part of the time at a substitution of 100% (9). At a substitution of 50%, the combination of chlorine and chlorine dioxide is more effective than either one alone, bleaching chemical cost is comparable to the cost of using pure chlorine, and effluent quality is improved. Increasing the substitution beyond 50% generally increases total chemical cost, and operation with 100% chlorine dioxide is significantly more expensive than with 50%. The reason for this is that pure chlorine dioxide does not delignify as effectively as pure chlorine or mixtures with chlorine.

Hypochlorite. Calcium hypochlorite *[7778-54-3]*, $Ca(OCl)_2$, was among the earliest chemicals to be used for bleaching pulp. Both calcium and sodium hypochlorite are cheap and capable of bleaching pulp to high brightness. Hypochlorite is still used, but its use is decreasing because the bleaching reaction generates chloroform *[67-66-3]*, $CHCl_3$, a by-product being strictly regulated by government agencies. Hypochlorite, is generally applied after chlorination and caustic extraction, for example in sequences such as CEHDED, CEHD, CEHEH, and CEHP. Aside from chloroform generation its chief drawback has been its tendency to degrade cellulose, especially if the pH is allowed to fall to values below about 8. Typical conditions are 1–4 h at 10–12% consistency, 30–40°C, and initial pH 11. Shorter times and higher temperatures may be used if the chemical application is tightly controlled. Chemical charge is normally in the range 0.5–1.5% as available chlorine. Future use of hypochlorite will be severely limited by restrictions on chloroform release.

Hydrogen Peroxide. Hydrogen peroxide *[7722-84-1]*, H_2O_2, has a variety of applications in chemical pulp bleaching (10). These include final brightening, addition, alone or with oxygen, to caustic extraction stages, and in a predelignification stage at the beginning of the sequence. Final brightening is the oldest application and can be done in a dedicated bleach tower, in a pulp storage tower, or in the pulp drying process. Addition of 0.5% or less raises final brightness 1–2 percentage points and significantly improves brightness stability. Typical tower conditions are 1–2 h, 80°C, pH 11, and 10% consistency, but milder conditions are used for storage tower bleaching. Addition of peroxide with oxygen to a first caustic extraction stage allows a significant decrease in the amount of chlorine used in the preceding stage. Addition to a second caustic extraction stage reduces chlorine dioxide consumption. Peroxide can be used to predelignify pulp but it usually does not compete well with oxygen in this application, because of its higher cost. Peroxide use will increase as efforts to displace chlorine continue.

Oxygen. The use of oxygen *[7782-44-7]*, O_2, with alkali to bleach chemical pulps was first practiced on a commercial scale in 1970 (11). Since then it has grown remarkably, as a result of continuing efforts by the industry to improve effluent quality. It was first used in a predelignification stage to remove about half of the lignin in the unbleached pulp. The resulting effluent can be recycled, concentrated, and burned in the chemical recovery system, because it contains no chloride ion or chlorine compounds. Oxygen predelignification is now becoming widespread and most new mills and mill expansions include it. In addition, the use of oxygen to enhance the effectiveness of the first caustic extraction stage has become nearly universal (12).

Predelignification with oxygen is conducted at either high (23–27%) or medium (10–12%) consistency. Nearly all of the early installations were designed for high consistency operation, to provide high interfacial area for efficient oxygen transfer, and a continuous gas phase to serve as an oxygen reservoir. The development of fluidizing, high shear mixers has since enabled the development of medium consistency systems. Oxygen is dispersed in the pulp as fine bubbles before it is fed to an upflow tower. These systems have a capital cost advantage over the high consistency ones because they do not require expensive dewatering equipment; as a result, nearly all newer installations have been designed for medium consistency operation. Delignification is limited to 40–50% to prevent pulp strength loss, because oxygen lacks the selectivity needed for more complete delignification. The addition of a magnesium salt as a cellulose protector helps in this regard. Oxidized kraft pulping liquor is normally used as a source of the alkali needed to promote the reaction. Typical conditions are 2.5% NaOH, 30 min, 500 kPa (5 atm), 110°C at 27% consistency, and 3% NaOH, 60 min, 500 kPa, 90°C at 12% consistency. Oxygen consumption is typically 2–3%.

Addition of oxygen to a first caustic extraction stage is usually achieved by dispersing oxygen in the pulp as it enters an upflow tower or preretention tube. An absolute oxygen pressure of 250 kPa, maintained for three minutes, is sufficient. Addition of 5 kg oxygen per ton of pulp allows the chlorine dioxide charge in a following stage to be reduced by 5 kg.

Ozone. Ozone *[10028-15-6]*, O_3, bleaching has been the subject of laboratory and pilot plant studies for many years but it remained uncommercialized until the announcement of the 1992 start-up of a full-scale plant at Union Camp's Franklin, Virginia mill. The laboratory studies have shown that ozone rapidly and extensively delignifies chemical pulps over wide ranges of consistency and other conditions (13). The two principal obstacles to commercialization have been selectivity and cost. Because ozone is such a powerful oxidizing agent it tends to be indiscriminate, so its application must be carefully controlled to prevent pulp strength loss. The cost is high because it must be generated on-site by passing pure, dry oxygen or air through a corona discharge, a process that consumes electrical energy and places high demands on the purification system for recycling unconverted oxygen in the spent ozone stream. Nevertheless, the growing demand for chlorine alternatives is likely to result in these problems being at least partially overcome and ozone bleaching will soon be a commercial reality. The selectivity and cost problems probably preclude direct replacement of chlorine, as in the ZEDED sequence, and favor combinations with other delignifying agents, as in the sequences OZED and O(DZ)ED (14). A likely scenario involves the use of ozone charges of less than 1%, high consistency, and ambient conditions.

Newer Developments. Research in progress points to the possible commercialization of several other chemical pulp bleaching technologies. These are chemical pretreatments to improve the selectivity of oxygen bleaching (15), enzymatic pretreatments to facilitate subsequent delignification (16), and recycling of bleach plant effluents. The first is best exemplified by the use of nitrogen dioxide pretreatment to extend the limit on oxygen delignification from 50% to 80% or perhaps higher. Although nitrogen dioxide does not itself remove appreciable amounts of lignin, it accelerates subsequent oxygen delignification reactions, with the result that less cellulose degradation occurs for a given degree of delignification. Problems remain, but the establishment of the principle may lead to eventual commercial use of this or some other selectivity-improving chemical pretreatment. Enzymatic pretreatments that selectivity remove hemicelluloses have been shown to result in significant reductions in oxidant requirements for subsequent delignification; hemicellulose removal may facilitate lignin removal by enlarging pores or by disrupting lignin–carbohydrate linkages. Finally, recovery and recycle of bleach plant effluents is the subject of considerable research. Environmental constraints on bleach plant discharges provide a growing incentive for this research, which also benefits from a full-scale mill closure experiment that lasted for several years at Great Lakes Forest Products in Thunder Bay, Ontario. One approach under investigation involves ultrafiltration of the effluent and incineration of the concentrate in a dedicated combustion unit (17).

Mechanical Pulp

Much new high yield pulping technology has been developed, including production of thermomechanical pulp (TMP) and chemithermomechanical pulp (CTMP). TMP is made by disk refining at elevated temperature and pressure. Under these conditions lignin softens, offering less resistance to fiber separation, and pulp of higher strength is obtained. CTMP carries lignin softening one step further by subjecting the wood chips to a mild chemical treatment, usually with sodium sulfite. Because little material is lost in these processes the pulps have a very high lignin content. Consequently, it is not

feasible to bleach them by removing all of the lignin, as in chemical pulp bleaching. Instead, the lignin must be decolorized, a process sometimes referred to as brightening, to distinguish it from lignin-removing bleaching methods. Only two brightening agents, hydrogen peroxide and sodium hydrosulfite (sodium dithionite), are of commercial importance (18).

Hydrogen Peroxide. Hydrogen peroxide *[7722-84-1]*, H_2O_2, is favored where brightness gains of more then 8–10 units are desired and the additional cost, relative to that of the cheaper hydrosulfite process, can be justified. Its effectiveness increases with increasing consistency so it is normally applied at medium (12% o) or high (25–30% o) consistency. An important variable is pH, which must be sufficiently high to ensure partial dissociation of the peroxide to its active form, the perhydroxyl anion, but not so high as to result in color-forming side reactions and excessive peroxide decomposition. An initial value of 10.5–11 is usually targeted. Decomposition can also be a problem within the optimum pH range, so sodium silicate *[1344-09-8]*, Na_2SiO_3, (2–4% o) and magnesium sulfate *[7487-88-9]*, $MgSO_4$, (0.05% o as Epsom salt) are added to inactivate traces of catalytic transition-metal ions such as iron, manganese, and copper. For the same reason, the pulp may also be pretreated with a chelating agent, usually diethylenetriaminepentaacetic acid (DTPA) *[67-43-6]*, $C_{14}H_{23}N_3O_{10}$, or ethylenediaminetetraacetic acid (EDTA) *[60-00-4]*, $C_{10}H_1 N_2O_8$. The bleaching is usually done in a tower at 40–60°C for 1–3 h and peroxide applications of 1–4% o are used. Alternatively, bleaching may be conducted by injecting the bleach liquor into the disk refiner where the pulp is made or by applying it to the pulp just prior to drying storage in partially dried (wet lap) form. Bleaching to high brightness requires high peroxide charges and unavoidably results in large amounts of residual peroxide in the spent bleach liquor. Where very high brightness is desired, as in some CTMP markets, multistage systems are employed to utilize the peroxide in the spent liquor. In one type, the pulp is prebleached in a first stage with spent liquor from the second stage.

Sodium Hydrosulfite. Reductive bleaching with sodium hydrosulfite *[7775-14-6]*, $Na_2S_2O_4$, is used when modest brightness gains (less than 10 units) are sufficient. An important consideration in applying hydrosulfite is its reactivity with oxygen; air must be excluded from the system to avoid loss of bleaching power. This is facilitated by operating at consistencies low enough (3–4% o) to ensure that air is not trapped in the pulp suspension. The effectiveness of hydrosulfite under these conditions is an advantage since it allows the bleaching to be conducted in available pulp storage vessels instead of a dedicated tower. Towers are nevertheless often used for the increased degree of control they provide. Temperature should be as high as possible and is usually maintained in the range 50–70°C for about 1 h. The pH should be close to 6.0. Brightness increases with increasing hydrosulfite charge up to about 1% o, beyond which no further benefit is obtained. One recent development in hydrosulfite bleaching technology is the use of high shear mixers to remove air and to mix the chemical with the pulp for bleaching at medium consistency. Another is in-refiner bleaching, which yields significantly higher brightness gains than the conventional tower process. Hydrosulfite is also sometimes used after peroxide in a two-stage process.

Hydrosulfite may be purchased as a proprietary formulation containing buffering and stabilizing agents, usually as a dry powder, but sometimes as a solution. The powder is pyrophoric and should be kept dry to avoid the possibility of fires. Alternatively, solutions of sodium hydrosulfite may be generated on-site by using a purchased solution of sodium borohydride and sodium hydroxide to reduce sulfur dioxide.

Economic Aspects

Recent estimates (19) of U.S. bleaching chemical costs are as follows:

Bleaching Chemical	$ ton
chlorine	100–260
caustic	180–380
chlorine dioxide	710–1841
oxygen	110–130
hydrogen peroxide	760–1200
sodium hypochlorite	370–540

As indicated by the wide ranges, the costs of some of these chemicals are region-specific, depending on, among other things, the cost of electrical power. Chlorine dioxide costs reflect the total cost of on-site generation. The cost of caustic is highly dependent on whether it is purchased together with an equivalent amount of its by-product, chlorine. Caustic purchased without chlorine, or "off-balance" caustic, is significantly more expensive. This cost difference is difficult to predict and may be understated by the above estimates. It is one of several factors that contribute to the relatively high costs of bleaching sequences that do not employ elemental chlorine.

An idea of the cost of bleaching chemical pulps may be gained from consideration of chemical requirements of an O(CD)(EO)D sequence, one of the many sequences now in use. The example assumes that this sequence is used to bleach softwood kraft having a residual lignin content of 5% o before the oxygen stage to a brightness of 88 ISO. Table 1 shows the amounts of chemicals in kg per air-dry (10% o moisture) metric ton (admt) of pulp that might be consumed for substitution of ClO_2 for Cl_2 in CD at 30 and 100% o.

Table 1. Estimated Chemical Cost of an O(CD)(EO)D Sequence

	ClO_2 substitution in CD	
Chemical, kg admt	30% o	100% o
oxygen	25	25
chlorine	25	0
caustic	35	22
chlorine dioxide	18	31
Estimated total chemical cost, $/admt	*36*	*50*

The cost is significantly higher when all of the chlorine is replaced by chlorine dioxide because the effectiveness of the latter as a delignifying agent is considerably less than that of mixtures of chlorine and chlorine dioxide. In addition, the decreased caustic requirement is negated by the additional unit cost of off-balance caustic.

The above example must be viewed in the context of the wide variability of bleaching costs that results from effects of wood species, the pulping process, the residual lignin content of the unbleached pulp, pulp quality requirements, the number of stages in the bleach sequence, and the region in which the bleach plant is located. For example, hardwoods (deciduous species) are generally easier to bleach than softwoods (coniferous species) and sulfite pulps are much easier to bleach than kraft pulps. Chemical pulp bleaching chemical costs may generally be expected to lie in the range of $25 to $75 per admt.

The costs of bleaching mechanical pulps are equally variable, especially in view of the variety of brightness targets associated with different grades, and the species dependence of the bleaching response. Spruce pulps destined for newsprint, for example, require only a few kilograms of hydrosulfite per ton for part of the time and bleaching costs may be in the range of $0–5 admt. Other applications, requiring brightness approaching 80% o ISO, may require two-stage peroxide–hydrosulfite systems with bleaching chemical costs in excess of $60 admt. Among the more difficult pulps to bleach are those made from jackpine and western hemlock. Pulps made from aspens, poplars, and cottonwoods are, in general, readily bleached.

Health and Safety Aspects

Because pulp bleaching agents are, for the most part, reactive oxidizing agents, appropriate precautions must be taken in their handling and use. For example, it is important to ensure that the threshold limit values (TLV) (20) in Table 2 are not exceeded in the workplace air. These are airborne concentrations in either parts per million by volume under standard ambient conditions or mg per cubic meter of air. They "represent conditions under which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse effect" (20). TWA refers to a time-weighted average for an 8-h workday; STEL is a short-term exposure limit or maximum allowable concentration to which workers can be continuously exposed for 15 minutes.

Table 2. Exposure Limits for Bleaching Chemicals

	TWA		STEL	
Chemical	ppm	mg/m^3	ppm	mg/m^3
chlorine	1.0	3.0	3.0	9.0
caustic		2.0		
chlorine dioxide	0.1	0.3	0.3	0.9
ozone	0.1	0.2	0.3	0.6
hydrogen peroxide	1.0	1.5	2.0	2.3

The toxicity of many bleaching chemicals is also reflected in observed effect doses and concentrations. These measures include lowest published toxic concentration (TC_{LO}), concentration that is lethal to 50% of a specified population (LC_{50}), lowest published lethal dose (LD_{LO}), and dose that is lethal to 50% of a specified population (LD_{50}). Some relevant values of these are listed in Table 3.

Table 3. Toxicity of Bleaching Chemicals

Chemical	TC_{LO} ppm	LC_{50} ppm	LD_{LO} ppm	LD_{50} mg/kg
chlorine	15[a]	293[b]	430[c]	
sodium hydroxide			500[d]	40[e]
chlorine dioxide	19[f]			
ozone	1[g]	5[h]		

[a] Pulmonary problems (human).
[b] For one hour (rat).
[c] For 30 minutes (human).
[d] mg/kg, oral (rabbit).
[e] eIntraperitoneal (mice).
[f] Inhalation (human).
[g] Pulmonary effects; 1.86 ppm for 75 min affects central nervous system; 100 ppm for 1 min affects skin (human).
[h] Inhalation for four hours (rat).

Other hazards associated with the use of pulp bleaching agents include their potential for damage resulting from contact with skin or eyes, their ability, as oxidizers, to cause fires or explosions upon contact with some kinds of organic matter or certain metals and inorganic compounds, and the possibility of explosive decomposition. Specific examples include the combustibility of titanium in an atmosphere of dry chlorine and the explosiveness of chlorine dioxide in air at concentrations greater than 10%. Hydrogen peroxide can cause explosions upon contact with organic matter and any one of a number of inorganic substances, including many metal oxides and sulfides. Ozone reacts with many compounds to start fires.

Additional information on health and safety aspects should be sought by consulting material safety data sheets available from suppliers of the chemical in question. In addition, most suppliers of bleaching chemicals, upon request, provide on-site training sessions by experts on the safe use and handling of their products.

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BLENDING.

See MIXING AND BLENDING.

BLOOD, ANIMAL.

See MEAT PRODUCTS.

BLOOD, ARTIFICIAL

Artificial blood is herein defined as consisting of red cell substitutes. Red cell substitutes are solutions intended for use in patients whose red cells are either not available or their use is to be avoided for other reasons. Despite enormous effort, more than 100 years of research have not produced a solution that can be used safely in humans.

In 1983 the move to develop red cell substitutes intensified when it was recognized that the acquired immune deficiency syndrome (AIDS) could be transmitted by the blood-borne human immunodeficiency virus (HIV). Concern for the nation's blood supply followed. Since that time other retroviruses have been identified, efforts to screen blood not only for these agents but also for viruses that cause hepatitis have intensified, the indications for transfusion have been reevaluated, and the use of blood products has become much more efficient. More careful screening of donors, testing of all donated units, and a general awareness in the donor population have all contributed to a decreased risk from transfusion-contracted AIDS.

The idea of red cell substitutes is not new. In Ovid's *Metamorphosis* the witch Medea restored Jason's aged father, Aeson, by slitting his throat to let out old blood, replacing it with a magic brew she had concocted (1). Sir Christopher Wren was one of the first to apply the new knowledge about circulation to blood substitutes. In 1656 he infused ale, wine, scammony, and opium into dogs and from these efforts conceived the ideal of transfusing blood from one animal to another. Lower actually carried out the first transfusion experiments (2).

Historical Blood Substitutes

Milk. Milk, one of the first materials to be used as a red cell substitute (3–7), was used in cases of Asiatic cholera in 1854. It was suggested that milk could regenerate white blood cells (3). Two patients were given 340 g or more of cow's milk and did well, but two others died (8). In all, twelve cases of injection of milk into the circulatory system were reported, and it was concluded that using milk in place of blood was a feasible, safe, and legitimate procedure. These results were met with excitement, and it was thought that milk injections would surplant the dangerous transfusion of blood (9). Milk was also shown to support function in isolated, perfused hearts from a variety of mammals (6). However, the transfusion of milk never gained widespread favor and soon disappeared from the literature.

Normal Saline. In the laboratory, the search for a red cell substitute was directed at understanding the physiologic role of blood and its many components. Some of the early work involved frogs. Salzfrosche frogs, where the blood was completely washed out and replaced with a pure sodium chloride solution, survived for some hours (10). Urea-frogs and sugar-frogs lived longer; if a small amount of red cells remained, they could survive indefinitely (11). But frogs are simple animals, and a frog's nervous system can be kept alive for some time without any circulation at all. Normal saline is, however, used widely as a plasma volume expander.

Ringer's Lactate. In 1883, it was discovered that the excised ventricle of the frog would beat for some hours if supplied with an aqueous solution of sodium, potassium, and calcium salts. The concentration of potassium and calcium was found to be critical, whereas the amounts of the anions had little effect on the frog heart. The composition of this saline, coined Ringer's solution, is given in Table 1. Many years later it was shown to be very close to that of frog plasma.

Table 1. The Composition of Ringer's Solution[a]

	Ringer's solution		
	g 100 ml	meq L	Frog plasma meq L
NaCl	0.6	102	104
KCl	0.0075	1	2.5
$CaCl_2$	0.01	1.8	1.0
$NaHCO_3$	0.01	1.2	25.4

[a] Ref. 12.

Ringer's lactate, in which lactate is added to Ringer's solution, is probably the most popular crystalloid (salt) solution for intravenous use in humans. The lactate is gradually converted to sodium bicarbonate within the body so that an uncompensated alkalosis is prevented (13). These crystalloid solutions cannot support life without red cells; saline passes rather quickly into the tissue spaces of various organs (14), especially the liver (15).

Gum-Saline. Gum is a galactoso–gluconic acid having molecular weight of approximately 1500. First used (16) in kidney perfusion experiments, gum–saline enjoyed great popularity as a plasma expander starting from the end of World War I. The aggregation state of gum depends on concentration, pH, salts, and temperature, and its colloid oncotic pressure and viscosity are quite variable. Conditions were identified (17) under which the viscosity would be the same as that of whole blood.

In early animal studies, gum was found to coat the surface of all blood cells and to promote coagulation. The use of gum–saline became popular in World War I. It was soon discovered that if the hematocrit was less than 25%, gum–saline was not efficacious in hemorrhagic shock. In the postwar period, it was shown (14) that gum–saline was not as efficacious in treating hemorrhagic shock as was saline alone, but gum–saline was useful in temporarily stabilizing blood volume (18). Through the 1920s many reports of anaphylaxis and other untoward reactions appeared, but it was claimed that when properly purified, gum–saline was safe for human use (19). Pharmacologic studies in the 1930s (19) showed that gum was deposited in the liver and spleen and could remain there for many years. Its half-life in the circulation was about 30 h, and anaphylaxis occurred occasionally. Success with gum–saline became common in the 1930s, but the need for it decreased with the increased availability of plasma.

Blood Plasma and Serum. The terms plasma and serum are frequently confused. Plasma refers to the liquid that suspends the red cells within the body. Serum is that liquid, removed from the body, from which the coagulum has been removed; serum contains no coagulation factors and is severely depleted of platelets.

As early as 1871 it was noted that frog hearts could be maintained by perfusion using sheep and rabbit serum (20), and that this solution was superior to 0.6% aqueous NaCl (21). Over ensuing years it was recognized that serum exerts a colloid osmotic pressure, contains bicarbonate, and may ensure capillary integrity. After dismissing a physiological role for plasma lipids, it was eventually agreed that albumin added to a balanced salt solution was superior to salt solution alone in maintaining the frog heart (5).

In the first half of the present century, much work was devoted to the study of plasma and serum as blood substitutes. One problem in this field was the recognition of toxic substances (22). Reports were published of intravascular coagulation and vasotonins that appeared mysteriously after the infusion of serum or plasma. It was suggested that this activity could be reduced by heating the serum or by filtering it before use. Platelets, insulin, and also adenosine triphosphate (ATP) were implicated. Once the red cell surface antigens were elucidated, the use of serum from donors of blood group AB markedly reduced the vasoconstrictor activity.

World War II ushered in the modern era of blood fractionation. It was shown that plasma could be administered directly to humans (23,24). Although cases of serum sickness frequently occurred five to seven days after the infusion, the procedure could be life-saving in cases of hemorrhagic shock (see FRACTIONATION, BLOOD) (25).

Albumin. Investigation into the safety of bovine plasma for clinical use was undertaken in the early 1940s in anticipation of wartime need (26). Using modern protein chemistry methods, including electrophoresis and ultracentrifugation, it was shown that most of the human adverse reactions to blood substitutes were caused by the globulin fraction and that albumin was safe for parenteral use. Human albumin is now used extensively as a plasma expander in many clinical settings.

Perfluorocarbons. In 1966, it was demonstrated (27) that a laboratory mouse could survive total immersion in a perfluorochemical (PFC) solution. This material, similar to commercial Teflon, is almost completely inert and is insoluble in water. A water-soluble emulsion was prepared that could be mixed with blood (28), and in 1968 (29) the blood volume in rats was completely replaced with an emulsion of perfluorotributylamine *[311-89-7]*, $C_{12}F_{27}N$. The animals survived in an atmosphere of 90–100% O_2 and went on to long-term recovery. However, the O_2 content of the perfluorochemicals has a linear dependence on the partial pressure of oxygen, P_{O_2}, as can be seen in Figure 1. The very high O_2 tension required to transport physiologic amounts of O_2 (12) and the propensity of the perfluorocarbon to be taken up by the reticuloendothelial cells were considered to be severe limitations to the development of clinically useful perfluorocarbon blood substitutes (30).

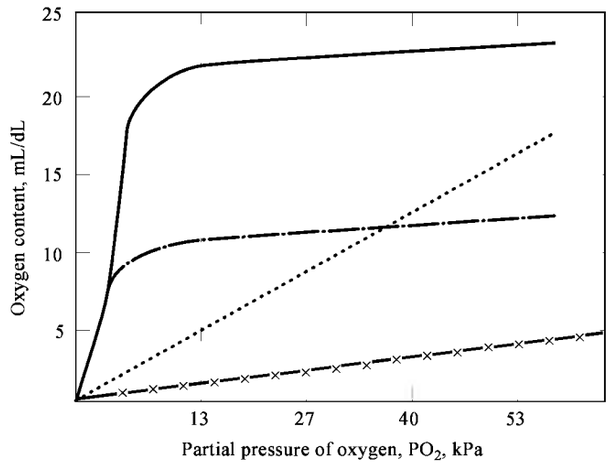


Fig. 1. Comparison of the oxygen capacity of (–) isooncotic blood (14 g/dL); (—·—) hemoglobin (7 g/dL); (×) a PFC emulsion (Fluosol); and (···) perflubron (——) represents the arterial oxygen partial pressure P_{O_2}. Note that the tetrameric structure of hemoglobin and its cooperativity lead to nearly complete saturation at the arterial oxygen partial pressure of 13 kPa (97.5 torr) (12).

For many years, the perfluorocarbons seemed to present insurmountable hurdles to further development. However, newer emulsions are being developed that allow higher concentrations of dissolved oxygen and interest in perfluorocarbon products has been renewed (31). One product, Fluosol-DA, a 20% by weight emulsion, has been licensed for use in coronary angioplasty. As of 1991, this product was available through the U.S. Food and Drug Administration (FDA) for compassionate use.

Cell-Free Hemoglobin. Hemoglobin seems to be the logical choice for a red cell substitute because of its high capacity to carry oxygen (Fig. 1) and its oncotic properties. Probably the first treatment of anemic patients with hemoglobin solution occurred in 1898 (32). Although the results were encouraging, stable solutions could not be prepared and the studies were not pursued further. Better preparations were reported in 1916 (33) when very small amounts of hemoglobin were administered in an effort to discover its renal threshold. No untoward reactions in 33 subjects were reported.

After these reports there were many attempts to administer hemoglobin solutions to humans. Many of these patients did well, but others demonstrated hypertension, bradycardia, oliguria, and even anaphylaxis. These untoward effects were not correlated with specific biochemical properties of the solutions themselves.

Modified Hemoglobin. Whereas interest in hemoglobin-based red cell substitutes remained extremely high, particularly in wartime, difficult problems impaired progress. First, hemoglobin in dilute solution is rapidly cleared by the kidney, as the tetrameric protein dissociates into smaller dimers. Second, dilute hemoglobin has a very high affinity for oxygen, so high that little of the bound oxygen is expected to be released in tissue capillary beds. Third, even exceedingly small amounts of stromal, ie, cell membrane, contaminants or endotoxin in hemoglobin solutions appear to be toxic.

The rapid disappearance of hemoglobin from the circulation was solved when it was discovered that cross-linking with bis(*N*-maleimidomethyl) ether (BME) prolonged plasma retention (34,35). It was concluded that cross-linking reduced the tendency to form dimers, and therefore the hemoglobin was not filtered by the kidney. Accordingly, it was shown that most of the hemoglobin could be found in various tissues and not in the urine.

The problem of the high oxygen affinity of cell-free human hemoglobin was solved when reagents were discovered that could bind to the 2,3-diphosphoglycerate (2,3-DPG) binding site and thus reduce the affinity for oxygen (36). This discovery led to a variety of hemoglobin modifications that not only reduce oxygen affinity but also stabilize hemoglobin tetrameric structure so that vascular retention is prolonged. The most widely used of these agents is pyridoxal 5′-phosphate *[54-47-7]* (PLP), $C_8H_{10}NO_6P$ (36).

In the 1960s it was believed that contradictory toxicity reports could be explained by contamination of the solutions with foreign materials. Novel ways to remove stroma from red cell hemolysates were studied, and the phrase stroma-free hemoglobin (SFH) was coined (37). These methods included filtration techniques that could be applied to large volumes of hemolysate and made possible physiologic studies in large animals. These results indicated that the toxic effects of hemoglobin might be prevented by rigorous purification.

Several pure hemoglobin solutions were later produced on a large scale for experimental use. A procedure was described for crystallization of hemoglobin and the product was evaluated in a series of animal trials (38–41). A 6 g/dL hemoglobin solution that had a P_{50} of about 2.4–2.7 kPa (18–20

torr) was produced and used in studies of tissue distribution (42) as was a similar solution of stroma-free hemoglobin that was used for many basic studies of O_2 transport (43) and for a clinical trial in humans (44). The term P_{50} corresponds to the partial pressure of oxygen at which 50% of the oxygen binding sites are filled.

The polymerization of proteins using the tissue fixative glutaraldehyde *[111-30-8]*, $C_5H_8O_2$, was described in 1973 (45). Soon, a process for polymerizing hemoglobin with the agent was patented (46), and this material demonstrated a markedly prolonged intravascular retention time. Although the reaction is extremely difficult to control, products for infusion have been developed (42,47,48). The most successful of these, PLP-polyhemoglobin, is obtained by reaction with PLP followed by polymerization with glutaraldehyde. This product was the first modified hemoglobin to be used in published human trials (49).

Many preparations of modified hemoglobin have been tested in animals. It appears that most are efficacious in transporting oxygen, and it seems that the more purified the solution, the less its toxicity. The nature of the specific modification appears to affect the biological properties such as plasma retention time, oxygen affinity, and colloid osmotic pressure, more than the toxicity. As of this writing, several hemoglobin solutions are approaching clinical trials.

Many variations of modified hemoglobin have been studied, including those stabilized using various types of cross-linkers. Some products are derived from hemoglobin conjugated to synthetic materials such as dextran *[9004-54-0]* or poly(ethylene glycol) *[25322-63-3]* and many are well into development as potential red cell substitutes. Sources other than human outdated blood also have been investigated. These include cow and recombinant hemoglobins produced in bacteria, yeast, and even transgenic mammals.

Encapsulated Hemoglobin. Because hemoglobin is normally packaged inside a membrane, encapsulated hemoglobin is thought to be the ultimate solution to the red cell substitute problem. In 1957 the use of microencapsulated hemoglobin as artificial red blood cells was reported (50). Since that time, dramatic results have been reported in the complete exchange transfusion of laboratory animals (51), but progress toward development of an artificial red cell for human use has been slow because of reticuloendothelial and macrophage stimulation problems (52). Other problems include maintaining sterility and endotoxin contamination.

Synthetic Heme. Synthetic compounds that bind or chelate O_2 have been produced. These compounds are commercially attractive because manufacture and licensure might be developed as a drug, rather than as a biological product. It has been shown that synthetic hemes can be used to transfuse animals (53). Although synthetic O_2 carriers would avoid the limited hemoglobin supply problem, the synthetic procedures are very tedious, and the possibility of scale up seems remote.

Hemoglobin Modifications

Reactivity. Hemoglobin can exist in either of two structural conformations, corresponding to the oxy (*R*, relaxed) or deoxy (*T*, tense) states. The key differences between these two structures are that the constrained *T* state has a much lower oxygen affinity than the *R* state and the *T* state has a lower tendency to dissociate into subunits that can be filtered in the kidneys. Therefore, stabilization of the *T* conformation would be expected to solve both the oxygen affinity and renal excretion problems.

The transition between the *T* and *R* states of hemoglobin is also deeply involved in the Bohr effect and cooperativity. Therefore stabilization of either of the two structures should diminish these effects, which have important physiologic consequences. The clinical consequences of stabilization are not known.

Stabilization of the *T* conformation under normal conditions is illustrated by the reaction of 2,3-diphosphoglycerate, (2,3-DPG) (Fig. 2). The negative charges on this polyphosphate form electrostatic, reversible interactions with eight positive charges on hemoglobin: two α-amino groups of valine NA1(1)β, two ε-amino groups of lysine EF6(82)β, and four histidines, NA2(2)β and HC3(143)β. In the *R* state the dimensions of the pocket change enough so that 2,3-DPG does not fit as well, and it drops out. Thus 2,3-DPG preferentially stabilizes the *T* conformation and has an overall effect of reducing oxygen affinity and increasing cooperativity. Analogues of 2,3-DPG, used to modify hemoglobin by forming permanent, covalent bonds, are variously effective, depending on molecular dimensions and charge. Some of the compounds react with only one of the reactive amino groups in the 2,3-DPG pocket; others react with all four.

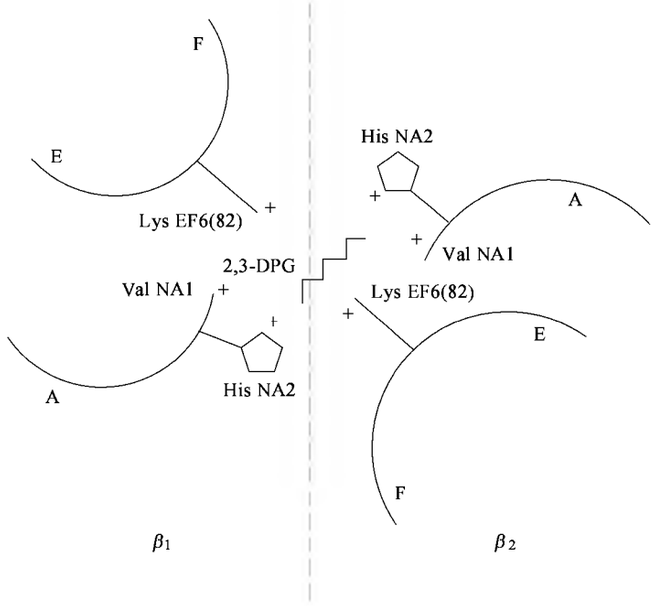


Fig. 2. Reaction of diphosphoglycerate (2,3-DPG) and deoxyhemoglobin. The molecule fits into the central cavity of hemoglobin and forms salt bridges with valine NA(1)β, histidines NA2(2)β, H21(143)β, and lysine EF6(82)β. A, E, and F correspond to specific hemoglobin helices and NA is the sequence from the amino-terminals to segment A.

In addition to the 2,3-DPG pocket, human hemoglobin contains 40 reactive lysines, ie, ε-amino groups, two α-chain *N*-terminal α-amino groups, and two sulfhydryl groups, ie, cystine F9(93)β. Most of the lysines are on the surface of the molecule, but some are internal, such as lysine G6(99)α. Thus the groups can be accessed by various cross-linkers and polymerizing agents, especially aldehydes. Although the lysine groups provide many potential sites for modification, their large number also means that such reactions are difficult to control.

All of the reactions considered to be useful in the production of hemoglobin-based blood substitutes use chemical modification at one or more of the sites discussed above. Table 2 lists the different types of hemoglobin modifications with examples of the most common reactions for each. Differences in the reactions are determined by the dimensions and reactivity of the cross-linking reagents. Because the function of hemoglobin in binding and releasing

oxygen is intricately connected to the transition between *T* and *R* conformations, it is not surprising that P_{50} and yield are highly variable. Even small differences among structures of the reagents can yield products having very different properties. In addition, the conditions of the reaction are very important, not only in regard to the state of ligation, ie, oxygen saturation, but also in regard to the presence of agents or molecules that block or compete for certain reactive sites.

Table 2. Classes of Hemoglobin Modifications[a]

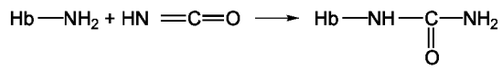
Class	Examples
amino-terminal modification	carbamylation, carboxymethylation, pyridoxylation, acetaldehyde
lysine EF6(82)β modification	mono(3,5-dibromosalicyl)fumarate
valine NA1(1)β-lysine EF6(82)β cross-link	2-nor-2-formylpyridoxal 5′-phosphate (NFPLP), bis-pyridoxal tetraphosphate (bis-PL)P_4
lysine G6(99)α_1–lysine G6(99)α_2 cross-link	bis(3,5-dibromosalicyl)fumarate
2,3-DPG analogue	pyridoxal 5′-phosphate
surface, multisite	glutaraldehyde, polyaldehydes, ring-opened dials, diimidate esters
conjugated hemoglobin	dextran–aldehyde, poly(ethylene glycol), polyoxyethylene

[a] Ref. 12.

A further complication of these reactions is that many nonhemoglobin proteins contain reactive groups and may also be modified to produce new, potentially toxic, contaminants. It has been difficult to produce a pure modified hemoglobin for toxicity studies because most processes start with relatively crude stroma-free hemoglobin.

Amino-Terminal Modification.

Carbamylation. Modification of the amino-terminal groups of hemoglobin (Hb) by the carbamylation reaction using isocyanic acid *[75-13-8]*



was used to show that valine NA1(1)α is one of the residues involved in the alkaline Bohr effect, and that the sickling of cells containing hemoglobin S could be inhibited specifically (54). It was also used to show the site of binding of carbon dioxide. The products of these reactions have increased oxygen affinity if the α-chains are carbamylated and decreased affinity if the β-chains are carbamylated. The carbamylation reaction held great promise in the control of sickling, but oral administration of sodium cyanate had toxic side effects. Additionally, extracorporeal carbamylation of hemoglobin and subsequent return to the patient proved to be impractical.

Carboxymethylation. Other modifications of the amino-terminal groups of hemoglobin have also been studied. It was reasoned that a covalent adduct at the amino-terminal amino group might reduce oxygen affinity by lowering or neutralizing the net positive charge in the 2,3-DPG pocket (55). Carboxymethylation using glyoxylic acid *[298-12-4]* followed by reduction with sodium borohydride *[16940-66-2]*, $NaBH_4$, resulted in a product that demonstrated lowered oxygen affinity and nearly intact Bohr and carbon dioxide effects (56). X-ray and nuclear magnetic resonance studies confirmed that the group introduced occupies nearly the same position as the naturally occurring carbamino group, ie, carbon dioxide adduct (57). It is expected that if this modified hemoglobin could be cross-linked further to reduce its dissociation and renal excretion, it might be very attractive as a blood substitute.

Acetaldehyde. Acetaldehyde *[75-07-0]*, C_2H_4O, has a slightly different reaction mechanism with hemoglobin (58). Although this reagent reacts with surface lysines under some conditions, the principal products are derivatives of the amino-terminal groups, both of the α- and β-chains. These products are not reduced with sodium borohydride and therefore do not involve an intermediate Schiff's base. Instead, a stable cyclic imidazolidinone derivative is formed. This reaction has not been developed further for use as a red cell substitute.

Pyridoxal Derivatives. Various aldehydes of pyridoxal (Table 3) react with hemoglobin at sites that can be somewhat controlled by the state of oxygenation (36,59). It is thereby possible to achieve derivatives having a wide range of functional properties. The reaction, shown for PLP in Figure 3, involves first the formation of a Schiff's base between the amino groups of hemoglobin and the aldehyde(s) of the pyridoxal compound, followed by reduction of the Schiff's base with sodium borohydride, to yield a covalently-linked pyridoxyl derivative in the form of a secondary amine.

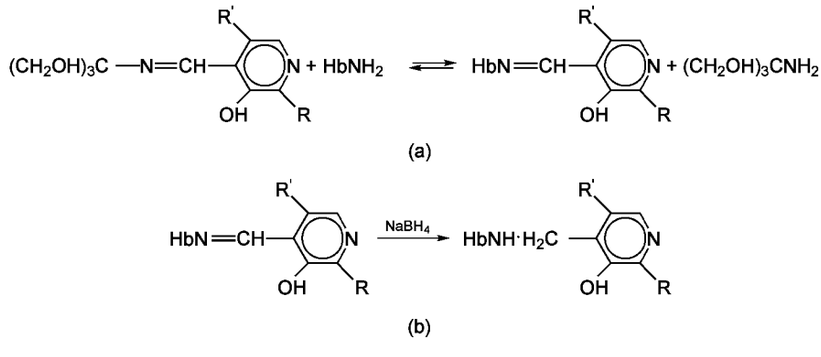


Fig. 3. (**a**) Reaction of pyridoxal 5′-phosphate (PLP) with an amino-terminal amino group of hemoglobin (Hb). The reagent is in the form of a Schiff's base with tris(hydroxymethyl)aminomethane *[77-86-1]* (Tris) buffer, and the reaction is a transamination. (**b**) The resulting unstable Schiff's base is reduced with sodium borohydride (12).

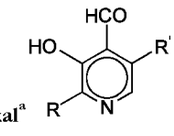


Table 3. Monofunctional Derivatives of Pyridoxal[a]

Compound	R	R′
pyridoxal	CH_3	CH_2OH

pyridoxal 5′-phosphate (PLP)	CH_3	CH_2-O-PO_3
pyridoxal 5′-sulfate (PLS)	CH_3	CH_2-O-SO_3
pyridoxal 5′-methyl-phosphonate (PMP)	CH_3	$CH_2-O-P(CH_3)O_2$
pyridoxal 5′-phosphatemonomethyl ester (PME)	CH_3	$CH_2-O-P(OCH_3)O_2$
5′-deoxypyridoxal (DPL)	CH_3	CH_3
2-nor-2-formylpyridoxal 5′-phosphate (NFPLP)	CHO	CH_2-O-PO_3

[a] Ref. 12.

Pyridoxal *[66-72-8]*, $C_8H_9NO_3$, has very little reactivity toward hemoglobin, but PLP *[54-47-7]*, $C_8H_{10}NO$ P, having a free phosphate in the 5′ position, reacts specifically with the amino-terminal groups of the β-globin chain in deoxyhemoglobin. The other reagents listed in Table 3 react with the amino-terminal groups of the α-globin chains in oxyhemoglobin.

The reaction of deoxyhemoglobin with PLP has been detailed (59). Pure diPLP-hemoglobin, hemoglobin having both β-chain amino termini modified, can be isolated by column chromatography. The structure of the product was confirmed by x-ray diffraction (60) and by peptide analysis (61). An electrostatic interaction of the 5′-phosphate with the 2,3-DPG binding site, lysine EF6(82)β, was also shown. Thus this modification closely mimics the action of 2,3-DPG in stabilizing the deoxy conformation.

The oxygen affinity of the derivative was shown to be about half that of unmodified hemoglobin under similar conditions, but a degree of cooperativity was preserved. Equilibrium and kinetic ligand-binding studies on this derivative have been interpreted (62) to show a perturbed *R* state. It is believed that although the reaction is between the two β-chains, αβ-dimers function independently, probably through a flexible connection.

The reaction of hemoglobin with PLP was scaled up (63,64) to batches of 20 L yielding from 70–80% modified hemoglobin. Methemoglobin could be kept at a manageable level (<10%), and the material was apparently unchanged after infusion into baboons. This solution was shown to be effective in resuscitation from hemorrhagic shock (65,66), but the plasma retention was thought to be too short and colloid osmotic pressure (COP) too high to be a definitive red cell substitute (67–69).

When the PLP reaction was explored in the absence of Tris buffer, it was found that reduction of the product with cyanogen borohydride produces a lower concentration of methemoglobin than does sodium borohydride but that both reagents yield a heterogeneous mixture of components (70). Heterogeneity of products also have been found (71,72) and it was reported that the P_{50} decreased on storage if the temperature is above 4°C. Some of the heterogeneity can be explained if exchange of αβ-subunits occurs (73).

Thus the large-scale preparation of pyridoxylated hemoglobin seems to result in mixtures of reaction products. These probably represent modifications at either or both α- and β-amino-terminal residues as well as surface lysines. A partial characterization of the mixture has been carried out (74).

Lysine EF6(82)β Modification. In 1989 a very interesting modification of human hemoglobin called a pseudocross-link was reported (75). In this reaction, hemoglobin reacts with the monofunctional reagent, mono(3,5-dibromosalicyl)fumarate, in oxygenated conditions. The product is specifically acylated at lysine EF6(82)β, in about 70% yield. Although cooperativity is reduced somewhat, ie, to a Hill coefficient of 2.0, the P_{50} under physiologic conditions is about 3.3 kPa (25 torr), and carbon dioxide binding is intact, because the sites for carbon dioxide binding are unaffected. It is of particular interest that the tetramer–dimer dissociation is retarded, possibly by stabilization at the β–β interface (76). The resulting plasma retention half-time in the rat is also prolonged by about fourfold for this acylated material, as compared to unmodified hemoglobin. This modification represents a new class of reactions that have potential for specificity and high yield.

Valine NA1(1)β–Lysine EF6(82)β Cross-Link.

2-Nor-2-Formylpyridoxal 5′-Phosphate. 2-Nor-2-formylpyridoxal 5′-phosphate, CHNOP, (NFPLP), of special interest because it contains two reactive aldehyde groups, reacts as shown in Figure 4 at two sites: at the amino-terminal group of one β-chain and at lysine 82 of the other (60,77). Thus in one modification reaction, this reagent both reduces the oxygen affinity of native hemoglobin and prevents its dissociation into αβ-dimers.

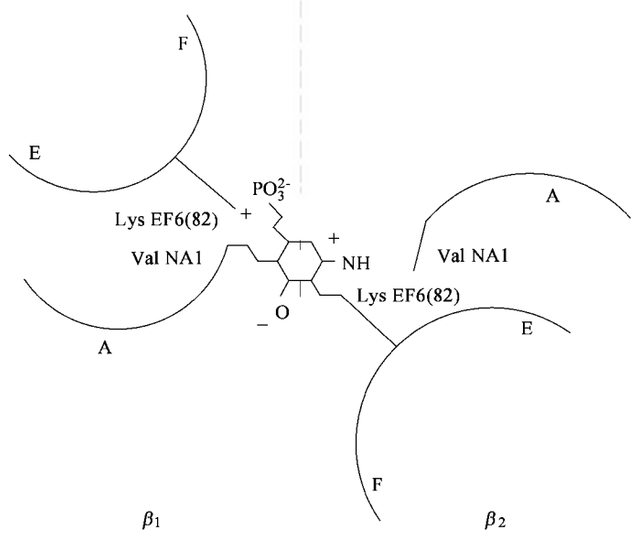


Fig. 4. Reaction of 2-nor-2-formyl pyridoxal 5′-phosphate (NFPLP) and hemoglobin (12). A, E, and F refer to helical areas; NA is the sequence from the amino-terminals to segment A.

NFPLP has been studied extensively. Because hemoglobin dimerization is prevented, NFPLP is not eliminated in the urine (78–80), and the plasma retention of the modified material is at least three times that of either unmodified hemoglobin (78) or pyridoxylated hemoglobin (81). Tissue distribution and elimination have been documented in detail (82–84). Accumulation of this modified hemoglobin derivative in the kidney is much reduced as compared to unmodified hemoglobin (84), and the oxygen affinity of the derivative under physiologic conditions is about 6.3 kPa (47 torr), with cooperativity retained. When used to perfuse isolated organs, the derivative supports a higher tissue oxygen tension in both the rabbit heart (85) and rat liver (86,87).

Although the 60–80% yield of the NFPLP product would be satisfactory for commercialization (88), the main drawback seems to be the difficulty

in preparation of the reagent (59). However a significant effort to develop this derivative as a potential blood substitute has been sustained (81,84,86–88).

Bis-Pyridoxal Tetraphosphate. A second class of bifunctional reagents, described in 1988, involves two pyridoxal groups linked by phosphates of different lengths (89). As shown in Table 4, the yield of intramolecularly cross-linked hemoglobin increases dramatically with increasing length of the phosphate backbone. It is believed that the site of reaction of (bis-PL)P_4 is between the amino-terminal amino group of one β-chain and the lysine 82 of the other β-chain, as for NFLP (89). However, the distance between these two residues is only 1.1 nm, and the reagent is much longer. Therefore it is concluded that the cross-linker must fold back upon itself to form a stacked pyridine ring conformation.

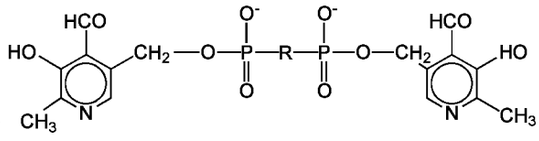


Table 4. Bis-Pyridoxal Polyphosphates[a]

Compound	R	% Tetramer
(bis-PL)P_2	O	16
(bis–PL)P_3	orthophosphate	18
(bis–PL)P_4	pyrophosphate	68
CH_2–(bis-PL)P_4	methylene diphosphate	53
fructose (bis–PL)P_4	fructose 1,6-diphosphate	41
PLP–DPG–PLP	2,3-diphosphoglycerate	70

[a] Ref. 12.

Further study of (bis-PL)P_4 modified hemoglobin (90) showed its P_{50} to be 4.1 kPa (31 torr) at pH 7.4, P_{CO_2} 5.3 kPa (40 torr) 37°C, with a Bohr effect about half that of unmodified hemoglobin. Its plasma retention is prolonged threefold in the rat, and there was no apparent toxicity in screening studies. These results suggest utility as a blood substitute. A great advantage of (bis-PL)P_4 is that its synthesis is much simpler than that for NFPLP. Thus the availability of (bis-PL)P_4 modified hemoglobin is not limited to laboratories having highly specialized equipment (91).

Other 2,3-Diphosphoglycerate Pocket Cross-Linkers. The reactivity of the valine NA1(1)α and lysine EF6(82)β residues in the 2,3-DPG pocket shown by NFPLP and (bis-PL)P_4 has stimulated the search for other reagents that react similarly but have potential for greater efficiency and ease of scaleup. The systematic study of four different dicarboxylic acid derivatives, cross-linked in both oxygenated and deoxygenated conditions, has been reported (92). Each of these derivatives presents problems in purification, and proof of the sites of reaction is tedious.

Lysine G6(99)α–Lysine G6(99)α Cross-Link. A class of bifunctional reagents that cross-link human hemoglobin has been described (93–96). The derivatives increased the oxygen affinity of native hemoglobin and were thought to have potential in preventing sickling in patients having sickle-cell anemia. When oxyhemoglobin was cross-linked using bis(3,5-dibromosalicyl)fumarate *[71337-53-6]*, (DBBF), $C_{18}H_8Br_4O$, the reaction site was shown to be between lysine EF6(82)β1 and lysine EF6(82)β2 (95). However, when cross-linking was carried out in deoxyhemoglobin, the α-chains were modified (97,98) (Fig. 5).

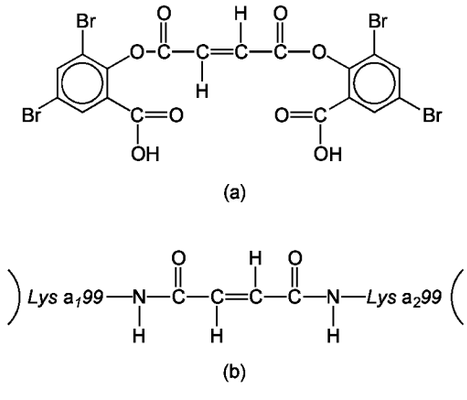
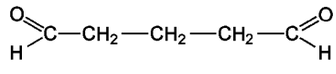


Fig. 5. Structures of (**a**) bis(3,5-dibromosalicyl)fumarate (DBBF) and (**b**) the α,α-hemoglobin cross-link (12).

In 1982 a study of the usefulness of DBBF in the production of a blood substitute was reported (99). A single modification achieved the dual goals of reduced oxygen affinity and restricted tetramer–dimer dissociation. This work was confirmed in 1987 (98). The product, called αα-hemoglobin, was formulated in Ringer's lactate. P_{50} under physiologic conditions is 3.7 kPa (28.0 torr), Hill's parameter is 2.2, and the Bohr effect was reduced (100). Plasma retention was increased, and the product appeared to be less heterogeneous than some of the other derivatives under study. Its production was scaled up by Baxter Healthcare Corp., under contract to the U.S. Army.

An interesting property of DBBF–hemoglobin is its thermal stability. This property has been used to achieve both a partial purification of the crude reaction mixture after cross-linking and inactivation of viruses in the final product (101,102).

Surface, Multisite Reagents. The addition of reactive groups to the surface of hemoglobin has been one of the most popular modifications because it results in large aggregates of molecules. These aggregates have the advantage of prolonging intravascular retention time. The disadvantage is that the extent of polymerization may be both nonspecific and difficult to control. The reagents are polyfunctional aldehydes. Glutaraldehyde is a prime example.



glutaraldehyde

Glutaraldehyde. Polymerization of pyridoxylated human hemoglobin using glutaraldehyde was first reported in 1980 (103). In the years that followed, this polyhemoglobin was studied intensively (48). A research team at Michael Reese Hospital in Chicago has commercialized a polymerization process and as of 1991 limited clinical trials have been carried out in humans. This process begins with pyridoxylated hemoglobin (14–16 g dL) that is then

polymerized using a 12.5% solution of glutaraldehyde. When the colloid osmotic pressure (COP) of the reaction mixture reaches normal values of 2.7–3.3 kPa (20–25 torr), the reaction is quenched by the addition of 1.3 *M* lysine. The resulting product has a distribution of molecular masses from 120,000 to 600,000, a P_{50} of 2.1 kPa (16 torr), a Bohr effect reduced by about half, and a Hill coefficient of 1.7. The viscosity is 4.5 mPa·s(cP) compared to that of 1.8 for unpolymerized hemoglobin. These solutions have no effect on coagulation, as measured by the prothrombin or partial thromboplastin times. As shown in Table 5, at equivalent COP, the polymerized solution has a higher hemoglobin concentration than that of native hemoglobin and therefore can carry more oxygen. Subsequent physiologic studies carried out using material of mol wt 124,835 (48) showed that the product transports oxygen as expected and that the reduced P_{50} did not diminish its usefulness (104). The plasma half-life of this product in baboons was remarkably prolonged, up to 46.2 hours, compared with 5.9 hours for PLP-hemoglobin (67).

Table 5. Properties of Pyridoxylated Polymerized Hemoglobin (PLP-polyHb)[a]

hemoglobin concentration, g dL		12 to 14
methemoglobin	<5%	
mol wt		64,000 to 400,000
mean molecular mass		150,000
P_{50}, kPa[b]	2.4	
n (Hill's parameter)		1.5 to 2.2
Bohr factor		0.12 to 0.25
colloid osmotic pressure, kPa[b]		2.7 to 3.3
viscosity, mPa·s (cP)		1.9 to 2.2
endotoxin, EU mL[c]	<0.625	
rabbit pyrogen test		pass

[a] Ref. 12.

[b] To convert kPa to mm Hg, multiply by 7.5.

[c] EU is an endotoxin unit.

Another procedure (64), using a crystallized hemoglobin as starting material (38,105) and a 7:1 molar ratio glutaraldehyde to hemoglobin with a hemoglobin solution of 14 g dL, did not include quenching the reaction. This study showed that the effects of PLP and glutaraldehyde on oxygen affinity are opposed: glutaraldehyde decreases P_{50}, but PLP increases it. A series of studies in a variety of animals has been reported (106) showing that this procedure could support life at zero hematocrit in rats and that its renal toxicity is minimal (107). An optimization study for the conditions of the reactions with PLP and glutaraldehyde was carried out and considerable batch-to-batch variability found (108).

Reexamination of the products of the glutaraldehyde reaction of pyridoxylated hemoglobin revealed extreme heterogeneity (108–111) and showed that the products are unstable on storage at 4°C; rearrangements of polymeric species occur so that it is difficult to prepare a predictably modified species. This heterogeneity and instability are regarded as serious drawbacks to the product because reactions with plasma proteins *in vivo* would be impossible to predict and toxicity would be difficult to understand. Concern has been raised (110) that the low molecular weight material might be preferentially lost through the kidneys, leaving the inherently less stable polymers with the less favorable oxygen transport properties.

Glutaraldehyde treatment of hemoglobin has the effect of making the tetrameric structure of the molecule more rigid. Indeed, it seems that the more highly modified the polymerized hemoglobin molecules are, the more rigid they become, as reflected by increasing oxygen affinity and decreasing cooperativity. Studies using the very sensitive Mössbaur technique (112) have shown that glutaraldehyde-treated hemoglobin has an increased rate of autooxidation and increased thermal stability. These properties could be explained by a weakening of the heme–globin linkage.

The heterogeneity of the glutaraldehyde product could make toxicology studies difficult. The heterogeneity results from chemical bonds that tend to rearrange. It is also conceivable that glutaraldehyde could leach out of the protein. Glutaraldehyde, known to leach out of materials used for prosthetic devices (113,114), is used as a tissue fixative and even small amounts of free glutaraldehyde have been found to have cytotoxic activity (115).

Other Polyaldehydes. A number of dialdehyde reagents can be prepared by oxidizing the ring structures of sugars or nucleotides (116). These reagents can react with hemoglobin at any of its amino groups and therefore form a variety of modifications including intramolecular and intermolecular links. One example of this type of modification involves opening the ring of inositol tetraphosphate. Another example, involves the opening of the pyridine ring of ATP (117) to form modified ATP–hemoglobin. This latter product was reported to have an elevated P_{50} and normal cooperativity.

Optimization of the ATP–hemoglobin reaction conditions produced a preparation having a markedly reduced oxygen affinity. Five fractions from a reaction mixture, when isolated, were found to have P_{50} values ranging from 1.1 to 5.0 kPa (8 to 38 torr), most with little cooperativity (118). These results are consistent with those found with other polyfunctional reagents that react on the surface of hemoglobin.

Diimidate Esters. Diimidate esters are bifunctional reagents that have been used in cross-linking a variety of proteins including hemoglobin. In a typical reaction, a lysyl ε-amino group reacts with the ester. The reagent is specific for surface ε-amino groups and forms polymers of varying size. One of the advantages of the reaction is that it replaces the $-NH_3^+$ group with a $=NH_2^+$ group, so the overall charge is unchanged. One reported product (119) had 30 of the 44 surface lysyl residues modified and had a molecular mass ranging from 68,000 to 600,000. Intravascular retention time was increased by about fourfold in rabbits.

Conjugated Hemoglobin. An alternative approach to prolongation of the plasma retention is to conjugate hemoglobin to a larger molecule. This was first done by coupling hemoglobin to dextran (120–123). The coupling reaction is carried out using a lysate of human red cells and bromodextran, molecular weight 20,000. The product was shown to support life in the absence of red cells in dogs (121–123) and cats (124), and it did not appear to be immunogenic (125). Because the oxygen affinity of dextran–hemoglobin was essentially that of hemoglobin, it was modified further by covalently linking an analogue of inositol hexaphosphate (126, 127). This new derivative had a P_{50} of 7.3 kPa (55 torr), compared to 3.1 kPa (23 torr) for dextran–hemoglobin, and the oxygenation curve showed cooperativity. The conjugated, right-shifted product was used to show that the modifications resulted in a reduction in renal toxicity of unpurified hemoglobin (128).

Hemoglobin also can be conjugated to other synthetic polymers such as inulin *[9005-80-5]* (129), poly(vinylpyrrolidinone) *[9003-39-8]*, $(C_6H_9NO)_x$, (130), and poly(ethylene glycol) *[25322-68-3]*, $(C_2H_4O)_nH_2O$, (131,132). One of the most studied of these conjugates is pyridoxylated hemoglobin–polyoxyethylene (PHP) (131). PHP has a molecular mass of about 90,000 and a P_{50} of about 2.9 kPa (22 torr), compared to 2.0 kPa (15 torr) for hemoglobin under the same conditions, but is has reduced cooperativity (133). The plasma retention half-life in dogs is about 36 hours, and it apparently causes no renal, hepatic, or coagulation toxicity. Histologic examination of the lungs and spleen of transfused dogs at two weeks and later showed no abnormalities (133).

Hemoglobin Sources

Purification. Hemoglobin is provided by the red blood cell in highly purified form. However, the red cell contains many enzymes and other proteins, and red cell membranes contain many components that could potentially cause toxicity problems. Furthermore, plasma proteins and other components could cause toxic reactions in recipients of hemoglobin preparations. The chemical modification reactions discussed herein are not specific for hemoglobin and may modify other proteins as well. Indeed, multifunctional reagents could actually couple hemoglobin to nonhemoglobin proteins.

Rabiner's method (37) for the filtration purification of hemoglobin was thought to be a significant advance over older centrifugation methods (134,135). However, hemoglobin prepared in this way still caused unwanted reactions in human recipients (44). The crystallization method (105) showed fewer toxic effects in animals (136), but batch-to-batch reproducibility was uneven (109). Ultrapurification of hemoglobin using ion-exchange chromatographic technique is possible but tedious and expensive (137).

Outdated Human Blood. If clinical efficacy and safety of hemoglobin solutions can be shown, the demand for product would soon outstrip the supply of outdated human blood. About 12 million units of blood (1 unit ≈ 480 mL) are used in the United States each year, and only about 500,000 outdate. The primary use of blood is in intraoperative and emergency settings. The quantity of blood available for use in production of blood substitutes depends on safety and efficient usage of blood products as well as on the demands on blood supplies.

Bovine Hemoglobin. One solution to the hemoglobin supply problem is to use as a starting material blood from nonhuman sources. For example, bovine hemoglobin is being developed for use. The ultimate success of bovine, or any other hemoglobin, depends on demonstration of safety, not supply. One problem in using bovine hemoglobin is the fear of bovine spongiform encephalitis (BSE) virus. This virus, related to the Scrapie organism, has been detected in cows in Europe, as well as other mammals in North America. Although there are no known human disease cases related to BSE, the FDA is concerned about bovine products of all types. This virus is especially resistant to heat treatment.

Bovine hemoglobin has certain desirable qualities for use as a blood substitute. Under conditions found in the red cell, it has a lower oxygen affinity than human hemoglobin because of its greater sensitivity to anions (138–141). Thus instead of regulation by 2,3-DPG, as is the case with human hemoglobin, bovine hemoglobin oxygen affinity is regulated by chloride ion.

Bovine hemoglobin has been cross-linked using the bifunctional reagent DBBF to obtain a product with a P_{50} in excess of 5.3 kPa (40 torr) under physiologic conditions (107). Although the reaction mixture was somewhat heterogeneous, no uncross-linked material was detected by sedimentation velocity analysis, and the plasma retention in rats was prolonged tenfold as compared to unmodified hemoglobin. It also has been found that the pyridoxylation reaction raises the P_{50} from 3.80 to 5.07 kPa (28.5 to 38.0 torr), and glutaraldehyde polymerization drops the P_{50} to 2.4 kPa (18 torr) (142). The polymerized material had essentially the same plasma retention time as human hemoglobin modified in the same way, and rats could also be supported at zero hematocrit.

Recombinant Hemoglobin. An alternative and novel source of hemoglobin for modification is from microorganisms the genome of which has been modified to contain globin genes for recombinant hemoglobin (rHb) production (see GENETIC ENGINEERING). Significant strides have been made in this approach, and it is possible to express both human α- and β-globin chains in *Escherichia coli* (143).

There are several problems with this approach. First, the yield is quite low: the best yield reported is about 0.1 g L of culture. Because one unit of blood (500 mL) contains about 15 g L of hemoglobin, a total of 75 g of hemoglobin equal to 750 L of cell culture would be needed. In the future it might be possible to express hemoglobin genes in higher organisms; synthesis of functional human hemoglobin has already been reported in mice (144). Another problem of rHb production involves purity. The product needs to be separated from media components and other microorganism products. Endotoxin contamination could be a serious problem for *E. coli* products, and low yield is an additional problem in yeast systems.

Status of Blood Substitutes

Several of the products discussed herein are under intense development. One product, based on recombinant hemoglobin, is in early human trials as of this writing. Other hemoglobin-based solutions are also under review at the FDA. Replacement of red blood cells using massive amounts of protein, free in solution, is an unprecedented therapeutic adventure.

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BLOOD, COAGULANTS AND ANTICOAGULANTS

The conversion of inert procoagulant glycoproteins to coagulant glycoproteins via proteolytic processing involves delicate balanced interaction between many different proteins, proteases, phospholipids, and the divalent cation calcium. The coagulation process can be activated and proceed through one of two possible sequential pathways: the intrinsic system path, components present within the circulating blood, and the extrinsic system, components present in the extravascular and intravascular compartment. Cooperative integration of these two systems, along with circulating platelets, maintains vascular integrity and preserves hemostasis.

The hemorrhagic diathesis in patients with coagulation disorders is because of either an abnormality of one or more plasma proteins and or platelets necessary for normal blood coagulation or the spontaneous presence of a circulating anticoagulant. Specific laboratory techniques are required for the precise identification of these disorders.

Biochemically, coagulation of the blood results from proteolytic processing of many different inert glycoproteins that originate in or migrate into the circulating blood (1–5). The participants in this complex process have been designated factors, and most have been assigned roman numerals. More recently identified participants in coagulation of the blood are designated by the name of the person who recognized the given factor, eg, von Willebrand protein, or by a name that indicates the composition of the substance, eg, high molecular weight kininogen. All factors listed in Tables 1 and 2 are present in plasma except III, and all are present in serum except for I, II, III, V, and VIII, though XIII is decreased to trace quantities Factor IIa (thrombic) may be present in serum. Factors I, VIII, and XIII are present in Cohn's fraction I; Factors II, V, VII, IX, X, XI, and XII are present in Cohn's fraction III; Factors II, VII, IX, XI, and XII are present in Cohn's fraction IX. Recently, the following not previously reported factors have been detected: Fletcher (prekininogenin [prekallikrein]), Fitzgerald (high molecular weight) kininogen (also designated as Williams or Flaujeac trait), and Passovoy (bleeding diathesis-prolonged partial thromboplastin time, normal known coagulation factors, autosomal dominant). Roman numerals have not yet been assigned to these factors. Factor VI is not listed in the tables because it is obsolete.

Table 1. Physical and Chemical Properties of Plasma Coagulation Factors

Factor (synonym)	CAS Registry Number	Protein type[a]	Molecular weight,[b] daltons	Isoelectric point	PPTA,[c] %
I (fibrinogen)	*[9001-32-5]*	GP	340,000	5.5	25
II (prothrombin)[d]	*[9001-26-7]*	GP[e,f]	73,000[g]	4.2	50
III (thromboplastin)	*[9002-05-5]*	LP	47,000		
IV (calcium)	*[14127-61-8]*		40		
V (proaccelerin, plasma acglobulin)	*[9001-24-5]*	GP	300,000		
VII (SPCA, proconvertin)[d,h]	*[9001-25-6]*	GP[e,f]	48,000–100,000[i]		50
VIII (antihemophilic globulin, AHG, antihemophilic factor, AHF)[h,j]	*[9001-27-8]*	GP	2,000,000[i]		33
VIII:vWFAg (von Willebrand protein)		GP[f]	30,000,000[i]		33
IX (plasma thromboplastin component, PTC, Christmas factor)[d,h]	*[9001-28-9]*	GP[e,f]	55,000–70,000[i]	4.50	50
X (Stuart-Prower Factor)[d]	*[9001-29-0]*	GP[e,f]	100,000[g]	5.5	50
XI (plasma thromboplastin antecedent, PTA)	*[9013-55-2]*	[f]	200,000[k]	4.50	33
XII (Hageman Factor)[l]	*[9001-30-3]*	Sialo-GP[f]	100,000[m]		50
XIII (fibrin-stabilizing factor)	*[9013-56-3]*		350,000[g]		33
Protein C_a[d]	*[42617-41-4]*	GP	102,000		40
Protein *S*[d]		GP	78,000		40
Protein Z		GP	62,000		40

[a] GP glycoprotein; LP lipoprotein.

[b] Of conjugated protein or of noted globulin.

[c] PPTA degree of saturation of $(NH_4)_2SO_4$ solution necessary for precipitation of factor.

[d] Synthesis is vitamin K-dependent.

[e] Adsorbed by $BaSO_4$ or $Au(OH)_3$ or $Ca_3(PO_4)_2$.

[f] Adsorbed by Celite (infusorial earth) or kaolin or carboxymethylcellulose (CMC).

[g] α-Globulin.

[h] Factor migrates in an electrophoretic field between α- and β-globulins.

[i] α-β-Globulin.

[j] Molecular weight of procoagulant subunit is ~200,000.

[k] β- or γ-Globulin.

[l] Factor migrates in an electrophoretic field between β- and γ-globulins.

[m] β-γ-Globulin.

Table 2. Biological Aspects of Plasma Coagulation Factors

	Deficiency state[c]

Factor	Synthesis site	Biological half-life, h	Volume of distribution, MPV[a]	Hemostasis concentration, %[b]	Per 10 population	Inheritance pattern[d]	Chromosome
I	liver	95–120	2.5	20	hypofibrinogenemia[e] or afibrinogenemia, <0.5	AR	4q26–q28
II	liver[f]	72	1.5–2.5	20	hypoprothrombinemia, <0.5	AR	11p11q12
III	all body tissues				not reported	AR	1pter–p12
IV							
V	liver	12–36	2	10–20	factor V deficiency, <0.5	AR	
VII	liver[f]	4–6	2–4	10	factor VII deficiency, <0.5	AR	13q34
VIII	hepatocytes	6–10[g] 15–18[h]	1–1.5	30–40	hemophilia A, 60–80	X-LR	xq28
VIII:vWFAg	vascular, endothelial cells, megakaryocytes	18–24	1–1.5	60	von Willebrand disease, 80–100	AD AR	12pter–p12
IX	liver[f]	6–10[g] 25–30[h]	2–3	30–40	hemophilia B Christmas disease, 15–20	X-LR	xq26–27
X	liver[f]	40–50	1	10–20	Stuart-Prower deficiency, <0.5	AR	13q34
XI	liver[i]	50–80	1	10–20	PTA trait, <1.0	AR[l]	
XII	liver	50–60			Hageman trait, <1.0	AR	5
XIII	liver[i], megakaryocytes	95–120	1–2	1–2	factor XIII deficiency, <0.5	AR	
Protein C_a	liver[f]	6–8	1–2	10–20	1–5	AR	
Protein S	endothelial cells[e]	42.5	1–2	10–20	<1	AR	
Protein Z	endothelial cells[e], hepatocytes	60	1–2	10–20			

[c] Condition in which coagulation factor level in a given patient is below the acceptable normal level.

[a] Multiples of plasma volume, ie, number given multiplied by plasma volume equals total volume in which the factor is located.

[b] The approximate concentration required to produce hemostasis, in percent of normal concentration.

[d] AD autosomal dominant; AR autosomal recessive; X-LR sex-linked recessive.

[e] Some pedigrees reported to have hypofibrinogenemia may be examples of dysfibrinogenemia; this condition is inherited as an autosomal dominant.

[f] Synthesis is vitamin K-dependent.

[g] Initial; the shorter initial half-lives for Factors VIII and IX are probably because of distribution into extravascular compartments.

[h] Secondary.

[i] Data are suggestive, but conclusive evidence is not yet available.

[l] Reported to be inherited both as autosomal recessive and as autosomal dominant.

Effective hemostasis is accomplished through an integrated sequence of vascular and intravascular functions. When the continuity of the vessel wall is broken, small arteries and veins normally undergo localized vasoconstriction, which impedes blood flow and facilitates the accumulation of platelets for subsequent formation of the platelet plug (6). The process of vasoconstriction appears to be a manifestation of neural reflexes involving the smooth muscles of arterioles and venules and is potentiated by biogenic amines released at the site of injury by aggregated platelets. Blood loss within fascial planes and closed tissue spaces may also be minimized by the extrinsic pressure exerted on the vessel following extravascular accumulation of blood.

Disruption of the endothelial surface of blood vessels expose collagen fibers and connective tissue. These provide surfaces that promote platelet adherence, platelet release reaction, and subsequent platelet aggregation. Substances liberated from the platelets stimulate further platelet aggregation, eg, adenosine diphosphate; maintain vasoconstriction, eg, serotonin; and participate in blood coagulation, eg, platelet Factors III and IV. In addition, the release reaction modifies platelet membranes in a manner that renders phospholipid available for coagulation. The thrombin *[9002-04-4]* elaborated by the coagulation mechanism is a potent agent in the induction of the platelet release reaction.

Stabilization and replacement of the platelet plug requires the participation of the blood coagulation system, which leads to the eventual formation of fibrin *[9001-31-4]*. Because most of the knowledge concerning blood coagulation has been gained under artificial *in vitro* laboratory conditions and then extrapolated to clinical settings, many gaps exist in the comprehension of the blood clotting mechanism. This complex system is usually conceptualized as either a waterfall (2) or cascade (5) to emphasize the sequential interactions of clot-promoting substances (Fig. 1). These schemes accommodate amplification and negative feedback mechanisms, provide the coagulation process with critical sites of control, and allow for interactions of end products and by-products with other systems, eg, activation of the kallikrein kinin system by fragments of coagulation Factor XII.

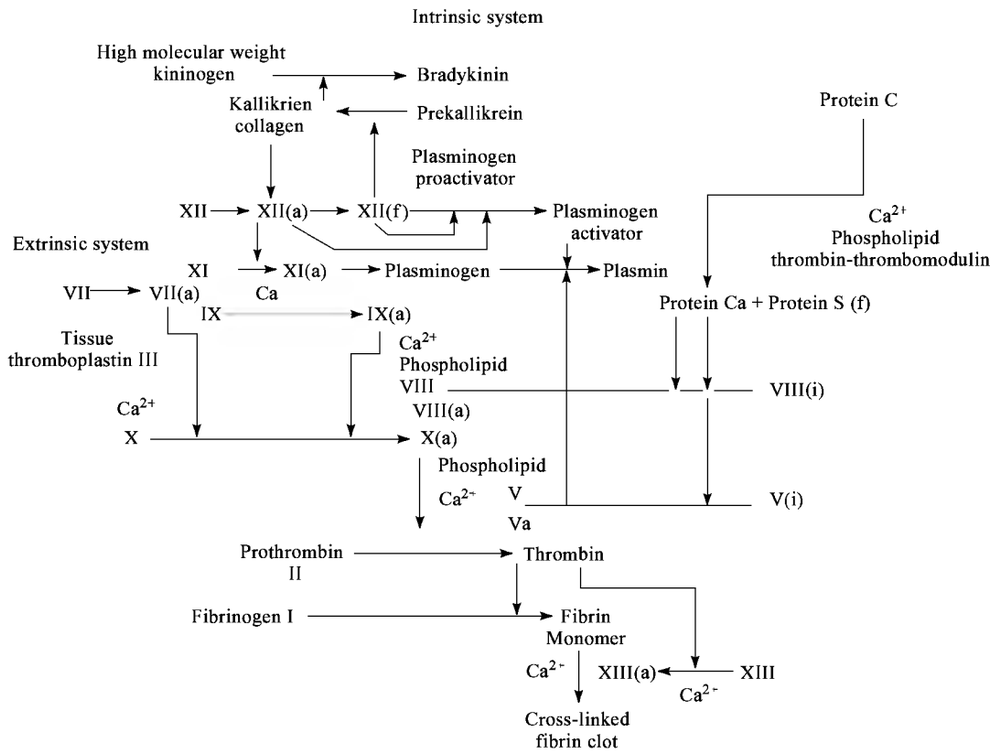


Fig. 1. Sequential interaction of clot-promoting substances where (a) designates active; (i), inactive; and (f), free.

Coagulation Process

The intrinsic and extrinsic system paths advance independently through their initial interactions but eventually follow a common course. The activity of both pathways are important *in vivo*. The concept of separate systems provides a practical means of evaluating laboratory and clinical coagulation abnormalities.

Extrinsic Pathway. Coagulation is initiated when tissue extracts with lipid–protein properties are released from the membranes of endothelial cells following injury or insult. These substances, collectively designated tissue thromboplastin, complex with circulating Factor VII and in the presence of calcium ions subsequently activate Factor X (Fig. 1). *In vitro* evidence suggests that Factor X can be activated less rapidly through the interaction of kallikrein *[9001-01-8]* with Factor VII.

Intrinsic Pathway. This system involves more protein–protein interactions and thus proceeds considerably slower than the extrinsic system. Intrinsic clotting initially was demonstrated *in vitro* by allowing plasma to clot in a glass test tube (7). It is now appreciated that the plasma component affected by the high negative charge of glass was Hageman Factor, Factor XII, a sialoglycoprotein with a molecular weight of 80,000 to 100,000 daltons. Activation is apparently accomplished without a change in molecular structure; however, conformational modifications are induced by *in vivo* activators of Factor XII, eg, collagen, endotoxin, platelet, and endothelial membranes, and by ellagic acid *[476-66-4]*, trypsin *[9002-07-7]*, or heparin *[9005-49-6]*. Whether prekallikrein *[9055-02-1]* (Fletcher Factor) and high molecular weight kininogen such as Williams, Fitzgerald, Flaujeac, and Reid Factors are needed to activate Factor XII *in vivo*, or whether they are needed for expression of the coagulant properties of Factor XIIa remains unclear.

Common Pathway of Coagulation. Factor X, Stuart-Prower Factor, activation can be accomplished by the products derived from either the intrinsic or extrinsic pathway (Fig. 1). As such, it represents the beginning of the common pathway of coagulation. *In vitro* assays are based on the direct conversion of Factor X to Factor Xa by proteases such as trypsin or Russell's viper venom. Factor X is a glycoprotein of molecular weight 55,000 daltons and is composed of two polypeptide chains, one heavy and one light. Activation is achieved by proteolytic cleavage of the heavy chain to yield Factor Xa, a serum protease inhibited by antithrombin III-heparin complexes produced during anticoagulation.

Prothrombin, or Factor II, is a single-chain glycoprotein with molecular weight 70,000 daltons. When activated, the prothrombin molecule undergoes proteolytic cleavage at two sites to yield a two-chain molecule linked by a disulfide bond. This new product is thrombin (Table 3). Although Factor Xa alone can convert prothrombin to thrombin, the participation of phospholipid and calcium ions in the presence of Factor V increases the rate of thrombin formation 100 times (12). The requirement for phospholipid may be instrumental in concentrating subsequent thrombin generation at sites where phospholipid from injured endothelial cells and adherent platelets will be available.

Table 3. Sequence Homologies for Serine Proteases Involved in Coagulation and Fibrinolysis[a,b]

Sequence homologies		References
	Amino-terminal sequence of the zymogens[c]	
prothrombin	Ala — Asn — Lys — Gly — Phe — Leu — Gla — Gla — ··· — Val — Agr — Lys — Gly — Asn — Leu	1
Factor IX	Tyr — Asn — Ser — Gly — Lys — Leu — Glu — Glu — Phe — Val — Arg — ··· — Gly — Asn — Leu	1
Factor X	Ala — Asn — Ser — ··· — Phe — Leu — Glu — Glu — ··· — Val — Lys — Gln — Gly — Asn — Leu	1
Factor VII	Ala — Asn — ··· — Gly — Phe — Leu — Gla — Gla — Leu — Leu — Pro — ··· — Gly	8
	Amino-terminal sequence of the β-chains of active enzymes	
thrombin	Ile — Val — Glu — Gly — Gln — Asp — ··· — Ala — Glu — Val — Gly — Leu — Ser — Pro — Trp — Gln	9
Factor IX_a	Val — Val — Gly — Gly — Glu — Asp — ··· — Ala — Glu — Arg — Gly — Glu — Phe — Pro — Trp — Gln	9

Factor X_a	Ile → Val → Gly → Gly → Arg → Asp → Cys → Ala → Glu → ··· → Gly → Glu → Cys → Pro → Trp → Gln	9
Factor XII_a	Val → Val → Gly → Gly → Leu → Val → ··· → Ala → Leu → Pro → Gly → Ala →? → Pro → Tyr → Ile	9
plasmin	Val → Val → Gly → Gly → Cys → Val → ··· → Ala → His → Pro → His → Ser → Trp → Pro → Tyr → Gln	10
Factor VII_a	Ile → Val → Gly → Gly	8
	Sequence of the active site[d]	
	180 185 190 195	
thrombin	Phe → Cys → Ala → Gly → Tyr → Lys → Pro → Gly → Glu → Gly → Lys → Arg → Gly → Asp → Ala → Cys → Glu → Gly → Asp → Ser → Gly → Gly → Pro → Phe	8
Factor IX_a	Phe → Cys → Ala → Gly → Tyr → His → ··· → Glu → Gly → Gly → Lys → ··· → ··· → Asp → Ser → Cys → Gln → Gly → Asp → Ser → Gly → Gly → Pro → His	8
Factor X_a	Phe → Cys → Ala → Gly → Tyr → Asp → → Thr → Gln → Pro → Glu → → → Asp → Ala → Cys → Gln → Gly → Asp → Ser → Gly → Gly → Pro → His	8
Factor XI	Val → Cys → Ala → Gly → Tyr → Arg → ··· → Glu → Gly → Gly → Lys → ··· → ··· → Asp → Ala → Cys → Lys → Gly → Asp → Ser → Gly → Gly → Pro →?	8
Factor XII	Leu → Cys → Ala → Gly → Phe → Leu → → Glu → Gly → Gly → Thr → → → Asp → Ala → Cys → Gln → Gly → Asp → Ser → Gly → Gly → Pro → Leu	8
plasmin[e]	Leu → (Gly → Ala) → His → Leu → Ala → Cys → Asn → (Gly → Gly → Thr) → → → → Ser → Cys → Gln → Gly → Asp → Ser → Gly → Gly → Pro → Leu	10
Factor VII	Phe → Cys → Ala → Gly → Tyr → Thr → → Asp → Gly → Thr → Lys → → → Asp → Ala → Cys → Lys → Gly → Asp → Ser → Gly → Gly → Pro → His	8

[a] All are bovine species, except plasmin (human).

[b] Gla: γ-carboxyl glutamic acid residues. (...) are used to bring sequences into alignment for greater homology.

[c] Sequences have been determined for plasminogen and bovine Factor XII, and they are not homologous with the other serine proteases. The amino-terminal sequence of Factor XII is homologous, however, with the active site of several naturally occurring protease inhibitors (11).

[d] Numbering corresponds to chymotrypsin with active serine at 195.

[e] The position of residues in parentheses was not definitely established. The second set has been reversed from that originally reported.

Thrombin, the two-chain derivative of the prothrombin molecule, has a molecular weight of approximately 37,000 daltons. Its proteolytic properties induce the conversion of fibrinogen to fibrin to produce the initial visible manifestation of coagulation, the soluble fibrin clot. In addition, thrombin influences the activity of Factors V, VIII, and XIII and plasmin. Thrombin affects platelet function by inducing viscous metamorphosis and the release reaction with subsequent aggregation.

Fibrinogen, Factor I, the primary target of the proteolytic activity of thrombin, is a dimeric glycoprotein consisting of three chains (Aα, Bβ, and γ) held together by disulfide bonds. Its molecular weight is 340,000 and its concentration in plasma is 300 mg dL, a level higher than any of the other proteins involved in the coagulation pathway. The letters A and B represent the fibrinopeptides located on the central amino-terminal ends of the alpha- and beta-chains respectively. These peptides are cleaved specifically by thrombin at arginine–glycine bonds to produce the gelatinous clot of soluble fibrin monomers (Figs. 1, 3).

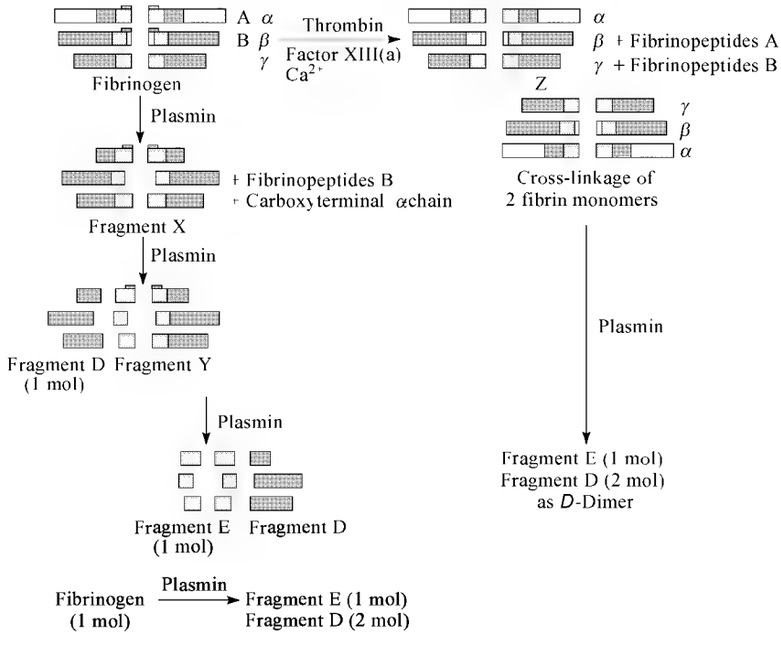


Fig. 3. Degradation products of fibrinogen fibrin.

The final phase of the coagulation cascade is stabilization and cross-linking of soluble fibrin monomers. This is accomplished by Factor XIII, fibrin stabilizing factor (Fig. 1). Factor XIII circulates as a zymogen composed of two pairs of different polypeptide chains, designated a and b. Intact Factor XIII possesses a molecular weight of approximately 350,000 daltons and is converted to its active transglutaminase form in the presence of both calcium ions and thrombin. Factor XIIIa catalyzes an irreversible amide exchange reaction between the γ-glutamine and ε-lysine side chains of adjacent fibrin monomers. This results in cross-linking between γ and γ-chains, γ and α-chains, and α and α-chains of fibrin. The clot structure is thereby strengthened and rendered insoluble in urea (5 *M*) or monochloracetic acid (1%).

Coagulation Factors II, III, VII, IX, X, XI, and XIIa fragments, thrombin, and plasmin are classified as serine proteases because each possesses a serine residue with neighboring histidine and asparagine residues at its enzymatically active site (Table 3). Factors II, VII, IX, and X, Protein C, Protein S, and Protein Z are dependent on the presence of vitamin K *[84-80-0]* for their formation as biologically functionally active procoagulant glycoproteins.

Factors I, II, III, V, VII, VIII, IX, X, XI, XII, and XIII, Protein C, and Protein S are synthesized in the liver. Factor III is present in many different organs throughout the body. Factor IV is the divalent cation calcium. The concentration of calcium required for normal function of the blood coagulation system is much less than required for normal physiologic function of many organs in the body, eg, myocardium.

Coagulation Factors

Factor I. Fibrinogen synthesized by the hepatocyte circulates in the blood as a soluble dimer consisting of three pairs of nonidentical chains Aα, Bα, and γ. When acted upon by the thrombin, two peptides designated A peptides are split (arginine–glycine) from the amino termini of the α-chains and two peptides are likewise split from the amino-termini β-chains, which initiates polymer formation with conversion to insoluble fibrin strands. Initially this occurs by end-to-end, then subsequently by side-to-side anastomotic bonding of fibrin tetramers, pentamers, hexamers, etc. The resultant fibrin strands form a lattice network that is the support structure for a thrombus. This structure, formed by process of tramsamidation of the γ–γ and γ–α chains, is rendered irreversibly insoluble by cross-linking.

Congenital deficiency of fibrinogen from the blood has been clinically recognized in three different forms: afibrinogenemia, complete absence of measurable fibrinogen, autosomal recessive disorder; hypofibrinogenemia, moderate-severe resolution in plasma fibrinogen levels to 20% of normal, all fibrinogen present is normal, autosomal dominant; and dysfibrinogenemia, defective fibrinogen molecule that does not respond normally to the proteolytic action of thrombin, autosomal dominant.

Factor II. Prothrombin is a vitamin K-dependent compound synthesized by the liver. When prothrombin is activated it is cleaved at two sites, resulting in a two-chain molecule linked by a disulfide bond that has a molecular weight of 37,000 daltons. Thrombin is the serine protease that initiates the conversion of soluble fibrinogen into fibrin.

Congenital deficiency of prothrombin is inherited in an autosomal recessive fashion and is the rarest of all the hereditary coagulation disorders. Congenital dysprothrombinemia has also been recognized.

Factor III. Tissue thromboplastin is a lipoprotein consisting of an apoprotein containing the antigen common to various organs and a phospholipid that is required for expression of thromboplastin activity. Factor III is a 47,000 dalton transmembrane glycoprotein that is an essential cofactor in the initiation of the extrinsic system by augmenting the proteolytic attack of Factor VIIa plus Ca^{2+} on Factors IX and X. It is ubiquitous in most body tissues but highest in concentration in the brain, lung, blood vessels, and placenta. No reported congenital or acquired deficiency of tissue thromboplastin exists.

Factor IV. Calcium ion, although essential, is required in only trace amounts for physiologic coagulation. Before such a decreased level could be attained, many other calcium-dependent body functions, such as myocardial contractility, would fail and death would ensue.

Factor V. High in sialic acid content, Factor V is a large asymmetric single-chain glycoprotein that becomes an active participant in the coagulation cascade when it is converted to its active form by α-thrombin. Approximately 25% of human Factor V is found in the whole blood associated with platelets. Factor V is an essential cofactor along with Factor Xa plus phospholipid plus Ca^{2+} in the conversion of prothrombin to thrombin.

Hereditary deficiency of Factor V is a rare autosomal recessive disorder. Combined deficiencies of Factors V and VIII have been identified in several families.

Factor VII. This is a vitamin K-dependent serine protease that functions in the extrinsic coagulation pathway and catalyzes the activation of Factors IX and X. Factor VII is present constitutively in the surface membrane of pericytes and fibroblasts in the adventitia of blood vessels, vascular endothelium, and monocytes. It is a single-chain glycoprotein of approximately 50,000 daltons.

Deficiency of Factor VII is relatively rare and inherited as an autosomal recessive disorder. Deficiency of Factor VII has been reported to be associated with bond abnormal bleeding and thrombotic tendencies. Deep vein thrombosis and pulmonary emboli have been reported in affected individuals. There is a very high frequency of Factor VII deficiency in people with the Dubin-Johnson syndrome, which is a congenital disorder of liver function.

Factor VIII. Originally known as antihemophilic globulin, Factor VIII is a very large glycoprotein complex of two different molecular units noncovalently linked. One unit is relatively lower in molecular weight at approximately 260,000 daltons and is the coagulant portion of the molecule designated VIII:C. This portion of the molecule is missing in classic hemophilia A (8,13–15). The larger portion of the molecule is approximately 3.1×10^6 daltons and composed of high molecular weight multimeric and oligomeric subunits. This very large portion of the Factor VIII complex is designated von Willebrand protein and also known as Factor VIII antigen (VIII:Ag or VIII:vWFAg) and ristocetin cofactor (16–18). This large multimeric protein functions as an adhesive protein in the coagulation cascade because of its capacity to bind to platelets at the GIb and GIIb-IIIa integral membrane receptor sites. It is now known that the VIII:C portion of the Factor VIII molecular complex is synthesized in the liver and the von Willebrand protein is synthesized by vascular endothelial cells and possibly megakaryocytes. Clearly, the Factor VIII complex is essential for normal coagulation, but its precise function in the intrinsic coagulation pathway remains unclear. The von Willebrand protein functions as the carrier protein for antihemophilic globulin (VIII:C) in a noncovalently bound complex. The efficiency of the Factor VIII complex as a participant in the intrinsic pathway is enhanced after it interacts with thrombin.

Deficiency of the VIII:C portion of the Factor VIII complex results in classic hemophilia or hemophilia A and is inherited as a sex-linked recessive disorder. Based on the degree of deficiency of the VIII:C molecule three different forms of hemophilia A are recognized. Less than 1% VIII:C activity equals severe hemophilia A. Two to 10% of normal VIII:C activity equals moderately severe hemophilia A. Ten to 25% of normal VIII:C activity equals minimal symptomatic disease. Deficiency of the VIII:vWFAg portion of the Factor VIII complex results in von Willebrand disease. There are at present five principal types of von Willebrand disease and numerous subtypes or variants. For the most part, von Willebrand disease is inherited as an autosomal dominant, and a few subtypes may be inherited as an autosomal recessive trait.

Factor IX. This factor is dependent on the presence of vitamin K for its activity as a biologically functional procoagulant glycoprotein. Factor IX is converted to its active form by XIa in the classic scheme of the intrinsic pathway. However, it can also be activated via interaction with Factor Xa or the complex Factor III plus Factor VII in the presence of calcium.

Congenital deficiency of Factor IX results in hemophilia B, also known as Christmas disease, and is inherited in a sex-linked recessive manner. Instructive is the fact that some female carriers are symptomatic. Combined deficiencies of Factors VIII:C and IX have been described.

Factor X. This is a vitamin K-dependent procoagulant glycoprotein whose activation can be accomplished by the activation products derived from either the intrinsic or extrinsic pathway. The activation of Factor X initiates the beginning of the common final path in the process of coagulation. Activation is achieved by proteolytic cleavage of the heavy chain of the Factor X molecule resulting in a serine protease that is sensitive to the inhibitory effect of heparin-antithrombin complex. This forms the rationale for the use of low doses of heparin to provide therapeutic anticoagulation. Activated Factor X or Xa is responsible for the conversion of prothrombin to thrombin, which is the last serine protease produced in the coagulation scheme.

Congenital deficiency of Factor X is a rare autosomal recessive disorder. Several variants have been described.

Factor XI. Factor XI is a liver-synthesized glycoprotein that circulates in a zymogen form as a dimer. It is converted to its active serine protease form by Factor XIIa in the presence of high molecular weight kininogen. Calcium is not required for this activation step.

Congenital deficiency of Factor XI is a relatively rare coagulopathy that has been reported as both an autosomal dominant and autosomal recessive trait. This deficiency state occurs predominantly in the Jewish population. Most patients with this deficiency state remain asymptomatic until trauma or surgery is encountered. Spontaneous hemorrhage is rare in this population.

Factor XII. This sialoglycoprotein is synthesized in the liver and is the site for initiation of the coagulent activity of the intrinsic pathway. Activation can occur by contact with a negatively charged surface. It is thought that prekallikrein and high molecular weight kininogen are *in vivo* cofactors in the activation of Factor XII. The proteolytic enzyme plasmin can cleave Factor XIIa into fragments that have activity in the conversion of XII → XIIa.

Congenital deficiency of Factor XII is inherited as an autosomal recessive trait. Deficiency of this factor is rarely associated with any coagulopathy. It has been observed that people deficient in this factor may have an increased frequency of thromboembolic complications.

Factor XIII. Factor XIII circulates in the blood as a zymogen composed of two pairs of different polypeptide chains designated A and B. Inert Factor XIII has a molecular weight of 350,000 daltons and is converted to its active transglutaminase form in the presence of thrombin and calcium. Activated Factor XIII, XIIIa, induces an irreversible amide exchange reaction between the γ-glutamine and ε-lysine side chains of adjacent fibrin

monomers. This results in insoluble and irreversible cross-linking between the γ–γ, γ–α, and α–α chains in fibrin. A single-chain form of Factor XIII may be produced in platelets.

Congenital deficiency of Factor XIII is inherited as an autosomal recessive trait and is frequently recognized at birth because of delayed persistent hemorrhage from the umbilicus. In Factor XIII-deficient people wound healing is defective and wound dehiscence is common.

Protein C. This vitamin K-dependent glycoprotein serine protease zymogen is produced in the liver. It is an anticoagulant with species specificity (19–21). Protein C is activated to Protein C_a by thrombomodulin, a protein that resides on the surface of endothelial cells, plus thrombin in the presence of calcium. In its active form, Protein C_a selectively inactivates, by proteolytic degradation, Factors V, Va, VIII, and VIIIa. In this reaction the efficiency of Protein C_a is enhanced by complex formation with free Protein S. In addition, Protein C_a activates tissue plasminogen activator, which promotes the conversion of plasminogen *[9001-91-6]* to plasmin *[9001-90-5]*.

Two types of hereditary Protein C deficiency have been recognized. In type I Protein C deficiency there is a defect in one of the genes coding for Protein C that will not permit translation. In these patients plasma Protein C activity and antigen are below the normal range, whereas the ratio of Protein C activity and Protein C antigen is within the normal range. In type II Protein C deficiency, one of the genes coding for Protein C has been modified, resulting in an abnormal gene product. In such patients the Protein C antigen is normal while Protein C activity and the ratio of activity to antigen are below the normal range. Protein C deficient heterozygotes and homozygotes are at high risk for venous thromboembolism involving peripheral veins, lungs, cerebral veins, and the microcirculation of the subcutaneous tissue. Protein C deficiency has been reported as an isolated deficiency state and combined with a deficiency of Factor V and Factor VIII:C.

Protein S. Protein S is a single-chain molecule of approximately 78,000 daltons that contains 10 γ-carboxy glutamic acid residues in the NH_2-terminal portion of the molecule. Protein S is a regulatory vitamin K-dependent protein. In plasma 40% of this protein circulates free and 60% circulates bound to C4b binding protein. Free Protein S functions as a nonenzymatic cofactor that promotes the binding of Protein C to membrane surfaces (22–25).

Two types of Protein S deficiency have been described. In type I deficiency there is little to no free Protein S but normal amounts of bound Protein S are present. In type II Protein S deficiency both free and bound Protein S are very low to absent. Deficiency of free Protein S is associated with venous and arterial thrombosis.

Coagulant Factor Replacement Therapy

The optimal technique for the treatment of hemorrhage associated with congenital factor deficiency states, including hemophilia A, hemophilia B, and von Willebrand disease, is intravenous replacement of the missing factor. This can be accomplished by the transfusion of whole blood, fresh–frozen plasma, cryoprecipitate, and factor concentrates. Depending on the circumstances and individual patient involved, one source of the necessary factor can be optimally selected. Because of the frequency of transmission of certain diseases by transfusion of these blood products, such as hepatitis A, hepatitis B, non A–non B hepatitis, hepatitis C, hepatitis delta, HIV, and additional rare viral and bacterial infections, there has been a recent concentrated effort to pasteurize these sources of coagulation proteins so that they are free of contaminants (26–28). These pasteurization purification techniques utilize methodology including monoclonal antibody specific selective separation of the factor from all other proteins in the plasma, dry and wet heat, solvent detergent, heat suspension in organic solvents, and molecular biologic recombinant expression of these individual proteins by mammalian cells. These techniques have been designed to produce safer, efficacious, more suitable, and less expensive factor replacement products.

Table 4 contains products available for Factor VII, Factor VIII:C (hemophilia A), Factor IX, and von Willebrand protein deficiency. Table 5 lists miscellaneous hemostatics and their proposed mechanisms of action.

Table 4. Products Available for Treatment of Specific Factor Deficiencies

Product name	Content[a]	Method of viral inactivation[b]	Manufacturer
	Factor VII		
Proplex-T	VII, rVII, VII, II, IX, X	DH 153 h at 60°C	Immuno, Novo,[c] Hyland[d]
	Factor VIII		
Coagulation Factor VIII-SD	VIII:C	SD	New York Blood Center[e]
Coagulation Factor VIII-SD	VIII:C	SD	American Red Cross
Monoclate-P	VIII:C	MA-DH	Armour
Hemofil M	VIII:C	MA-SD	Hyland
AHF-M	VIII:C	MA-SD	American Red Cross
Humate-P	VIII:C	AHP 10 h at 60°C	Behringwerke[f]
Koates-HS	VIII:C	AHP 10 h at 60°C	Cutter[g]
Koates-HP	VIII:C	SD	Cutter
Profilate-OSD	VIII:C	SHP 20 h at 60°C	Alpha
Koate HT	VIII:C	DH	Cutter
Cryoprecipitate	VIII:C VIII:vWFAg Fibrinogen Plasminogen Factor XIII		American Red Cross
Fresh–frozen plasma	all coagulation factors, r VIII:C		American Red Cross
Autoplex-T	IIa, VIIa, IXa, Xa	DH	Hyland, Immuno
FEIBA	VIIa		
	Factor IX		
Konyne-HT	IX, VII, X, II	DH 72 h at 68°C	Cutter
Proplex-T	IX, VII, X, II	DH 153 h at 60°C	Hyland
Proplex SX-T	IX, X, II	DH 153 h at 60°C	Hyland
Profilnine	IX, X, II	SHP 20 h at 60°C	Alpha
Alphanine	IX, X, II	MA-SD-AHP	Alpha
	von Willebrand Factor products		
Cryoprecipitate	VIII:vWFAg VIII:C, Fibrinogen Plasminogen Factor XIII		American Red Cross

[a] Coagulation factors; r indicates recombinant.

[b] AHP anhydrous heat pasteurized; DH dry heat; MA moist atmosphere; SD solvent detergent; SHP solvent heat pasteurized.

[c] Novo Nordisck AS, Copenhagen, Denmark.

[d] Hyland Division Baxter Healthcare Corp., Glendale, Calif.

[e] New York Blood Center Melville Biologics, Inc., a division of the New York Blood Center, Melville, N.Y.

[f] Behringwerke is distributed by Armour Pharmaceutical, Blue Bell, Pa.

[g] Cutter Miles, Inc. Westhaven, Conn.

Table 5. Miscellaneous Topical[a] Hemostatics and Action Mechanisms

Preparation	Trade name	Mechanism	Manufacturer
carbazochrome salicylate	Adrenosem[b]	reduce capillary permeability	SK Beecham Pharmaceutical
oxidized cellulose	Oxycel	support structure clot formation	Parke Davis
gelatin sponge	Surgical	support structure clot formation	Johnson & Johnson
gelatin sponge	Gelfoam	support structure clot formation	Upjohn Co.
microfibrillar collagen	Avitene	induce platelet aggregation	Alcon Laboratories
topical thrombin	Thrombin	induce fibrin polymerization	Parke Davis
fibrin glue	Tisseel	support structure clot formation	Immuno
desmopressin	DDAVP[c]	increase concentration of von Willebrand protein	Rhone-Poulenc Rorer
conjugated estrogens	Premarin[c]	induce hormone balance	Wyeth-Ayerst

[a] Unless otherwise noted.

[b] Oral or intramuscular administration.

[c] Intravenous administration.

Anticoagulants

***In Vitro* Anticoagulants.** A number of substances have been identified that prevent coagulation of the blood when it is removed from the vascular compartment of the body. Most of these substances remove a vital constituent of the blood that is essential in the mediation of transformation of liquid blood into a solid.

Ethylenediamine tetraacetic acid (EDTA) *[60-00-4]* (Sequestrene), an anticoagulent at 1 mg of the disodium salt per mL blood, complexes with and removes calcium, Ca^{2+}, from the blood. Oxalate, citrate, and fluoride ions form insoluble salts with Ca^{2+} and chelate calcium from the blood. Salts containing these anticoagulants include lithium oxalate *[553-91-3]* $Li_2C_2O_4$, 1 mg mL blood; sodium oxalate *[62-76-0]* $Na_2C_2O_4$, 2 mg mL blood; potassium oxalate monohydrate *[6487-48-5]* $K_2C_2O_4 \cdot H_2O$, 2 mg mL blood; sodium fluoride *[7681-49-4]* NaF, 2 mg mL blood; trisodium citrate *[6132-04-3]* $C_6H_5Na_3O_7$, 0.42 mg mL blood; sodium polyanetholesulfonate *[52993-95-0]* (Liquoid), 1–2.5 mg mL blood; and heparin *[9041-08-1]* a micropolysaccharide (*vide infra*), 0.1 unit mL blood.

Plasma Inhibitors, *In Vivo* Anticoagulants. Fourteen naturally occurring compounds that normally exert an inhibiting effect on the activity of coagulation, platelet function, and fibrinolytic activity and complement systems have been identified within the circulating blood.

α_1-Antichymotrypsin	C-1 Esterase inhibitor
α_1-Antiplasmin	Inter α-trypsin inhibitor
α_2 Antiplasmin	Plasminogen activator inhibitor-1
α_1-Antitrypsin	Plasminogen activator inhibitor-2
α_2-Antiactivator	Protein C
α_2-Macroglobulin	Protein S
Antithrombin III	Protein Z

These naturally occurring inhibitors modulate the activity of the systems or metabolic pathways involved in hemostasis. The inhibitory effects of these agents are not specific for a single compound or biochemical pathway as their name would suggest, eg, antithrombin III is not only inhibitory against the effect of thrombin, but it is also inhibitory against the plasminogen–plasmin proteolytic enzyme system. α_1-Antitrypsin is inhibitory against trypsin but also inhibits the action of tissue plasminogen activator. The inhibitory effect of antithrombin III (AT-III) is enormously enhanced by complex formation with small amounts of heparin when this polyanionic molecule combines with the cationic lysine residues of AT-III.

Pathologic inhibitors (circulating anticoagulants) of the normal hemostatic mechanism (29,30) rarely appear spontaneously in the plasma. These circulating anticoagulants include the prevalent IgG immunoglobulins (γG_4 most common) and the rare IgM or IgA. These inhibitors appear in approximately 10–15% of patients with congenital factor deficiency states, but also appear in the elderly (60–90 yr). In the latter, these inhibitors are not associated with any recognized illness. The presence of these anticoagulants is associated with severe hemorrhage. A third group of individuals has recognized inhibitors that occur in association with diseases of connective tissue and a wide variety of different disease states. In this group of individuals the inhibitor, designated Lupus-like Inhibitor, is not associated with clinical hemorrhage but paradoxically may be associated with thrombosis (9).

Therapeutic Anticoagulants.

Heparin. One of the most unique and therapeutically useful medications of all time, heparin *[9041-08-1]* was discovered incidentally by sophomore medical student, Jay McClean in the autumn of 1915 (10). Originally extracted from dog liver and myocardium, heparin is a highly sulfonated mucopolysaccharide, a glycosaminogluconan, consisting of a heterogenous series of repeating disaccharide units composed of D-glucuronic or L-iduronic acids in a 1,4-glycosidic linkage to glucosamine. Each of the repeating units contains two sulfate esters and one *N*-sulfate group (11,31–35). Heparin is the strongest anionically charged organic acid substance ever isolated from a living biological system. This substance can be found in many different body tissues, but the lung, intestinal tract, liver, and mast cells are particularly rich in concentration. It is a family of linear polymers that differs in chain length and molecular weight, and its precise complete composition is unknown.

Commercially, heparin is extracted from animal tissues and most commonly from bovine lungs and the intestinal mucosa (the alimentary tract and all organs attached) of bovine, ovine, porcine, and caprine species. In any vial of therapeutically employed heparin, a wide range of molecular species ranging from 2,000–25,000 daltons are present. The potency of heparin is defined in units, where one unit is the amount of heparin that will prevent the coagulation of sheep plasma by the process of recalcification. Various extracts of heparin may range in potency, ie, 1 mg by weight may range in potency

from 80–170 units. International reference standards are maintained by the World Health Organization.

Heparin exerts its inhibitory effect on the coagulation cascade scheme by at least two different mechanisms. First, when heparin complexes with antithrombin III (AT-III) at high affinity lysine residues in a 1:1 stoichiometric manner, the serine protease inhibitory effect of AT-III is enhanced several fold. Second, because of its high polyanionic charge density, heparin has impressive capacity to neutralize the effect of positively charged activated glycoprotein coagulant serine proteases. Heparin also exhibits a number of different actions in the body including induction of lipoprotein lipase, antiinflammatory properties, and induces histaminase degradation of histamine.

Heparin has been widely employed since the mid-1940s as a clinically useful therapeutic agent in the treatment of a variety of different disease entities. Its main utility has been in the prophylactic prevention and treatment of thrombotic diseases such as deep vein thrombosis, pulmonary emboli, and myocardial infarction. A second principal and critically important use of heparin is to prevent blood coagulation in extra-corporeal systems and thus facilitate the possibility of renal dialysis; cardiac bypass surgery (cardiac valve repair and replacement, coronary artery bypass and repair, myocardial repair); cardiac, pulmonary, hepatic, and renal transplantation; extra-corporeal pulmonary bypass oxygenation; and extra-corporeal circulatory membrane ultrafiltration. Low doses of the lower molecular weight species are employed for the prophylactic prevention of intravascular thrombus formation. Recently, very low molecular weight heparin fragments, peptides, or synthetically prepared peptides have been therapeutically employed.

Coumarinic Acid Compounds. These synthetic phylloquinone derivatives and congeners have been employed as anticoagulants since the isolation of 3,3′-methylenebis(4-hydroxy-2*H*-1-benzopyran-2-one) *[66-76-2]* (bis-4-hydroxycoumarin or dicoumarol) (**1**) from spoiled sweet clover in 1939. The ingestion of the latter was responsible for widespread and extensive death of bovine animals at that time. The parent compound for the synthesis of many congeners is 4-hydrocoumarin, which is synthesized from methyl salicylate by acetylation and internal cyclization. The basic structures of these compounds are shown in Figure 2, and their properties listed in Table 6 (see COUMARIN).

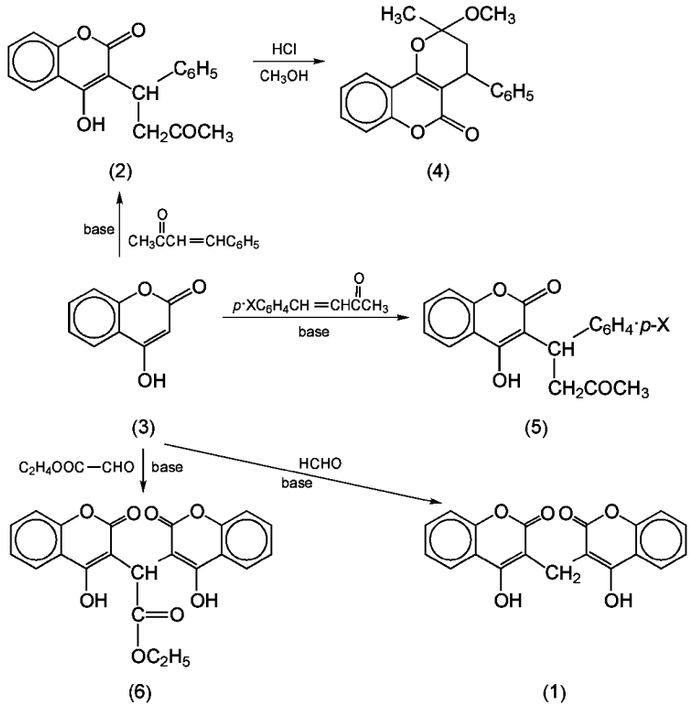


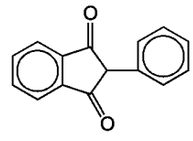
Fig. 2. Synthesis of coumarin derivatives (see Table 6).

Table 6. Properties of Coumarinic Acid Anticoagulants

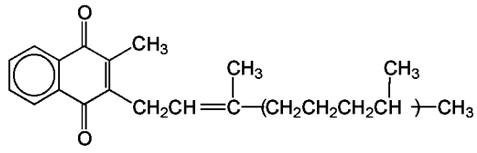
Name	CAS Registry Number	Structure number	Molecular formula	Melting point, °C
bis-4-hydroxycoumarin	*[66-76-2]*	**1**	$C_{19}H_{12}O_6$	287–293
warfarin	*[81-81-2]*	**2**	$C_{19}H_{16}O_4$	161
4-hydroxycourmarin	*[1076-38-6]*	**3**	$C_9H_6O_3$	213–214
cyclocumarol	*[518-20-7]*	**4**	$C_{20}H_{18}O_4$	166
acenocoumarin	*[152-72-7]*	**5** (X = NO_2)	$C_{19}H_{15}NO_6$	196–199
coumachlor	*[81-82-3]*	**5** (X = Cl)	$C_{19}H_{15}ClO_4$	164–165
ethyl biscoumacetate	*[548-00-5]*	**6**	$C_{22}H_{16}O_8$	177–182 154–157[a]

[a] Dimorphous.

In contrast to heparin, the coumarinic acid anticoagulants are inactive *in vitro;* like heparin they are active *in vivo.* The phenylindanedione-type compounds (7) (36) and warfarin (**2**) produce their *in vivo* inhibitory effect on the coagulation system by competitively antagonizing the normal activity of vitamin K_1 (8) (37–44).



(7)



(8)

Vitamin K normally catalyzes the addition of the second carboxyl group on the gamma carbon of glutamic acid in those procoagulant glycoproteins containing glutamine residues. In the presence of warfarin the attachment of the second carboxyl group does not take place and the glutamic acid residue cannot bind Ca^{2+}, without which the coagulation protein is not biologically functional. Thus those procoagulant glycoproteins that are dependent on vitamin K for their normal function, Factor II, VII, IX, X, Protein C, Protein S, and Protein Z, are devoid of functional activity and the coagulation cascade scheme is rendered dysfunctional.

New Therapeutic Anticoagulant Agents. There are some patients who cannot receive heparin or warfarin but who need anticoagulation. To deal with this need, appreciable investigation is in progress to identify new anticoagulants. Several such agents are on the horizon.

Hirudin *[8001-27-2]* is a polypeptide of 66 amino acids found in the salivary gland secretions of the leech Hirudo medicinalis (45). It is a potent inhibitor of thrombin and binds to γ-thrombin with a dissociation constant of 0.8×10^{-10} *M* to 2.0×10^{-14} *M*. Hirudin forms a stable noncovalent complex with free and bound thrombin completely independent of AT-III. This material has now been cloned and expressed in yeast cells (46,47). Its antigenic potential in humans remains to be established.

Arvin *[9046-56-4]* is a purified fraction from the crude venom of Agkistrodon rhodostoma (48). The action of this venom fraction is selectively specific for fibrinogen and can rapidly deplete fibrinogen *in vivo* safely from the circulating blood. Blood without fibrinogen cannot undergo clot formation.

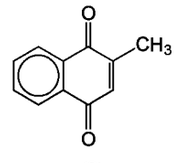
Activated Protein C (C_a) *[42617-41-4]* (19–21) is a naturally occurring serine protease that, in combination with free Protein S, degrades and inactivates Factors V, Va, VIII, and VIIIa. By degradation of these factors the blood becomes anticoagulated and thus C_a may be a useful therapeutic agent.

Argatroban *[74863-84-6]* ((2*R*,4*R*)-4-methyl-1-[N^2-)(3 methyl 1,2,3,4-tetrahydro-8-quinolinesulfonyl)-L-arginyl]-2-piperidinecarboxylic acid monohydrate) is a potent inhibitor of thrombin formation and activity (49). This agent has been studied *in vitro* and in a few animal models. Its toxicity and activity in humans are unknown.

Brodifacoum *[56073-10-0]* is a substituted 4-hydroxywarfarin with a strikingly prolonged half-life in the human body (50,51). Although used as a rodenticide, it has been ingested by some humans and observed to persist from 50 days to eight months. Its use in humans may be prohibitive because of the excessively prolonged half-life in the body.

Anticoagulant Antagonists. Heparin, because of its high polyanionic charge density, is highly negatively charged and can be readily neutralized by polycation substances that are positively charged. A number of polycationic substances can be employed. Protamine sulfate *[9009-65-8]* is most commonly employed as a heparin antagonist. This substance is derived from mature sperm of salmon and other species of fish, with a molecular weight of 8,000 daltons. It consists of 58 amino acids, 40 of which are arginine. One mg of protamine sulfate will neutralize approximately 100 units of heparin, depending on the source of the heparin. Protamine sulfate must be administered to humans with considerable caution because excessive quantities can induce precipitation of several procoagulant and other plasma proteins. Other heparin antidotes include polybene, cluppein, polylysine, lyozyme, toluidine blue, fuchisin, tryptophan, and indocyanene green.

Vitamin K can antagonize coumarinic acid compounds (warfarin and its congeners) and indandione derivatives. Vitamin K exists in several forms including simple water-soluble menadione *[58-27-5]* (9)



(9)

and lipid-soluble K_1 (8) and its 2,3-oxide *[25486-55-9]* mephyton, which contains a phytyl side chain on the basic nucleus. Only the latter (oxide) compounds efficiently antagonize warfarin and its congeners. The simple menadione forms can correct for nutritional deficiency states but will not effectively antagonize warfarin-type compounds.

The Fibrinolytic System

The human fibrinolytic system is a proteolytic enzyme system consisting of several components found in different locations in the body including the blood, vascular endothelium, and several tissues extrinsic to the vascular compartment (52,53). The central component of the human fibrinolytic system is plasminogen synthesized by the liver and present in the euglobulin fraction of the blood. This inert precursor or proenzyme can be activated by an agent intrinsic to the blood designated proactivator that is converted to an activator by the combined interaction of prekallikrein, high molecular weight kininogen, kallikrein, and Factor XIIa. The action of the activator on plasminogen yields the potent proteolytic enzyme plasmin. Another path of activation that is intrinsic to the body but extrinsic to the blood originates in the vascular endothelium. The agent released by the vascular endothelium, designated vascular plasminogen activator, is capable of direct activation of plasma plasminogen, independent of the blood activator. Additional agents extrinsic to the vascular compartment, designated tissue plasminogen activators, have been extracted from the uterus, pancreas, lung, kidney, and prostate. The activity of all these endogenous activators is normally modulated by several intrinsic naturally occurring inhibitors. Activation of the human plasminogen–plasmin proteolytic enzyme system is also achieved by a variety of exogenous agents from several different sources including bacteria, fungi, synthetic substances, and human urine. The fibrinolytic system in humans occupies several vital positions not only in the removal of intravascular fibrin-thrombi but also participates in other biological functions including ovulation, embryo implantation, neoplastic transformation, tissue repair, and macrophage function.

Conversion of Plasminogen to Plasmin. Plasminogen is the circulating zymogen which, upon activation, yields the fibrinolytic enzyme plasmin. The principal production site of plasminogen, like most other plasma proteins, is the liver. The plasma concentration of plasminogen in adult humans remains constant at about 200 mg mL (2.2 m*M*). Native plasminogen has a plasma half-life of about two days and disappears primarily through catabolic degradation rather than conversion to plasmin or intravascular consumption.

Plasminogen is inherited as two codominant autosomal alleles. Fetal synthesis and the absence of transplacental passage have been demonstrated. In newborns there is a decrease in both plasma plasminogen concentration, and functional plasminogen activity, suggestive of a fetal dysfunctional plasminogen molecule. Several hereditary dysfunctional molecules have been described in adults with recurrent thromboembolic disease. The defects in these molecules include abnormal active sites, impaired activator binding, and defective activation.

The isolation of human plasminogen has demonstrated a remarkable degree of microheterogeneity of the molecule (54). Plasminogen is usually purified from serum or plasma using affinity chromatography. Plasminogen is absorbed onto a column of lysine–sepharose and eluted with ε-aminocaproic acid. Using this technique, two plasminogen variants having different amino termini have been isolated: A native form containing glutamine at its NH_2-terminus (Glu-plasminogen), and a modified form containing lysine at its NH_2-terminus (Lys-plasminogen). The modified Lys-plasminogen has been

shown to be a partial degradation product of native Glu-plasminogen and is formed during the isolation process by contaminating plasmin. The lysine residue at the amino terminus of Lys-plasminogen corresponds to Lys_{77} in the amino acid sequence of Glu-plasminogen. The properties of Lys- and Glu-plasminogen differ markedly. The plasma half-life of Glu-plasminogen is two days, whereas the half-life of Lys-plasminogen is 0.8 days.

Additional isolation techniques can separate plasminogen into many microheterogeneous forms. Using either polyacrylamide gel electrophoresis at acidic pH or affinity chromatography, two different forms of plasminogen, (Type 1 and Type 2 differing in carbohydrate content) can be distinguished. Polyacrylamide gel electrophoresis at alkaline pH further separates plasminogen Types 1 and 2 into at least five subtypes. Using isoelectric focusing, Glu-plasminogen can be further separated into four isoelectric forms with isoelectric points ranging from 6.2 to 6.6. Lys-plasminogen can be further separated into five isoelectric forms with isoelectric points from 6.7 to 8.5.

Isolation of native human plasminogen has also led to the determination of its molecular structure and biochemical properties (55). The plasminogen molecule is a single-chain glycoprotein having a molecular weight of between 83,000 and 93,000 daltons and the electrophoretic mobility of a beta-globulin. The primary amino acid sequence of the molecule has been elucidated and is 790 amino acids long, with glutamine at its amino terminus and asparagine at its carboxy terminus. There are a total of 48 cysteine residues forming 24 disulfide bridges; 16 of these bridges are located in five looped structures known as kringles. These structures, numbered K1 through K5, contain about 80 residues each and are held together by triple disulfide bonds. Homologous kringles can be found in the nonthrombin part of the prothrombin molecule.

The carbohydrate portion of plasminogen, which comprises about 2% of the molecule, accounts at least in part for its microheterogeneity (56). Plasminogen Type 1 contains two oligosaccharide side chains, a glucosamine-based chain at ASN_{288} and a galactosamine-based chain at Thr_{345}. Plasminogen Type 2 contains only the single galactosamine-based chain at Thr_{345}. In addition, the proportion of various sugars differs between the two types. Type 1 contains more sialic acid, galactose, mannose, and *N*-acetylglucosamine than Type 2.

The secondary structure of the plasminogen molecule, as determined by circular dichroism spectra, is 80% random coil, 20% beta-structure, and 0% alpha-helix. Electron microscopy has demonstrated the tertiary structure of plasminogen to be a 22- to 24-nm long spiral filament with a diameter of 2.2 to 2.4 nm.

The conversion of plasminogen to plasmin by plasminogen activators is accomplished by proteolytic cleavage of a single bond, Arg_{560}–Val_{561} (57). Two chains are thus formed: the A or heavy chain is derived from the NH_2-terminus of plasminogen, while the B or light chain originates from the COOH-terminus. The molecular weights of the A and B chains are 60,000 and 25,000 daltons, respectively. The A chain has only one isoelectric form (pI 4.9), whereas the B chain has three isoelectric forms ranging between pI 5.8 and 6.0. The A and B chains are connected by two disulfide bridges at Cys_{547}–Cys_{605} and Cys_{557}–Cys_{595}. The Cys_{547}–Cys_{605} bond is homologous to the interchain disulfide bonds of chymotrypsin, thrombin, and Factor X. The activator-sensitive Arg_{560}–Val_{561} is located within the Cys_{557}–Cys_{595} disulfide bridge, which is unique to plasmin and appears to facilitate the interaction between activator and cleavage site.

Although the precise mechanism of plasminogen activation is unknown, three principal theories have developed based on studies of the *in vitro* activation of native human plasminogen. Activation of native Glu-plasminogen in the absence of any plasmin inhibitor yields Lys_{77}–plasmin plus the so-called pre-activation peptides (PAP) formed by cleavage at Lys_{62}–Ser_{63}, Arg_{67}–Met_{68}, or Lys_{77}–Lys_{78}. Activation takes place by a two-step mechanism in which both the release of the PAPs from the NH_2 terminal of Glu-plasminogen, and the subsequent cleavage of the Arg_{560}–Val_{561} bond are catalyzed by the activator. When aprotinin *[9087-70-1]*, a synthetic plasmin inhibitor, is present to prevent any plasmic autodigestion, Glu-plasmin is the final end product by way of a one-step transformation of Glu-plasminogen to Glu-plasmin. Subsequent PAP fragment removal could occur by excess plasmic autodigestion. It has been proposed that the PAPs are first released by plasmic autodigestion to form the intermediate Lys_{77}–plasminogen, which is subsequently cleaved by activator at the Arg_{560}–Val_{561} bond to form Lys_{77}–plasmin.

The plasminogen molecule contains several sites that specifically bind a number of antifibrinolytic amino acids, such as lysine *[56-87-1]* and ε-aminocaproic acid *[60-32-2]* (EACA). These sites are known as lysine binding sites (LBS), and are localized mainly to the A or heavy chain of the molecule. One is located in K4 and at least one more is in K1 through K3. One LBS, which is believed to reside in K1, has a stronger affinity for EACA, whereas the others have a weaker affinity. The LBS are important for the interaction of plasminogen with several components of the endogenous fibrinolytic system.

The weak LBS are involved in the interaction of plasminogen with plasminogen activators. Both loss of the preactivation peptides from Glu-plasminogen and binding of the antifibrinolytic amino acids causes a conformational change in the plasminogen molecule that makes the Arg_{560}–Val_{561} bond more easily accessible for cleavage by activator. Kinetic data on the activation of both native Glu-plasminogen and modified Lys-plasminogen are consistent with facilitation of activation by removal of the PAP. Although the Michaelis-Menten constants for both forms are similar (K_m 23 m*M* for Glu-plasminogen and K_m 40 m*M* for Lys-plasminogen), the catalytic constant is ten times greater for Lys-plasminogen (0.26 s^{-1} vs 2.6 s^{-1}).

The high affinity LBS is involved in the interaction of plasminogen with fibrin, α_2-antiplasmin, and a plasmin inhibitor called histidine-rich glycoprotein. It has been observed that plasminogen activation takes place on the surface of fibrin and that α_2-antiplasmin competitively inhibits the plasminogen–fibrin interaction at the high affinity LBS.

The B or light chain of plasmin contains the proteolytic active site of the molecule, and is homologous in both structure and mode of action to other proteases, including thrombin, Factor Xa, and the pancreatic proteases. The active center is formed by three amino acid residues, His_{602}, Asp_{645}, and Ser_{740}. The serine residue is sensitive to diisopropyl fluorophosphate (DFP), whereas the histidine residue is sensitive to tosyl lysine chloromethyl ketone (TLCK). Plasmin functions as an endopeptidase with an optimum pH of about 7.0. It acts specifically as a serine protease, cleaving only synthetic esters and amides of lysine and arginine and peptide bonds having either lysine or arginine on the carboxyl side of the molecule.

The kinetic data for the action of plasmin on different substrates under various conditions have been summarized. The Michaelis-Menten constant (K_m) varies between 10 and 1000 m*M* and the catalytic constant between 1 and 75 s^{-1}.

Action of Plasmin on Fibrin and Fibrinogen. Fibrin is the principal physiologic substrate of plasmin. Other elements of the coagulation cascade, including Factor VIII, Factor V, and fibrinogen, are inactivated by plasmin. The human fibrinogen molecule has a molecular weight of about 340,000 daltons and consists of three pairs of nonidentical peptide chains represented by the formula $(A\alpha B\beta\gamma)_2$. When the coagulation system is activated, thrombin cleaves the A and B fragments from fibrinogen, yielding the fibrin polymer $(\alpha\beta\gamma)_2$. Activated Factor XIII subsequently cross-links the fibrin polymers to form an insoluble fibrin clot.

The actions of plasmin on both fibrin and fibrinogen have been studied extensively. Plasmin cleaves fibrin and fibrinogen into a family of fragments known as fibrinogen and fibrin (FDP-fdp) degradation products.

The fibrinogen degradation products are known as fragments X, Y, D, and E; X and Y are intermediate fragments; and D and E are terminal core fragments (Fig. 3). Fragment X has a molecular weight of 262,000 daltons and is generated by cleavage of the COOH-terminal of the Aα-chain. Specific bond cleavage sites have been identified. Removal of the COOH-terminal sections of the Aα-, Bβ-, and γ-chains of X fragment results in fragment Y with a molecular weight of 170,000 daltons. Subsequent cleavage at the Lys_{62}–Ala_{63} bond of either the X or Y fragment yields the D fragment. The D fragment can be further modified to three subforms having molecular weights ranging between 83,000 and 93,000 daltons. The E fragment, also formed from the cleavage of X or Y, contains the NH_2-terminal fragments of all six fibrinogen chains and has a molecular weight of somewhere between 50,000 and 63,000 daltons.

The degradation of fibrin by plasmin is more complex because the fibrin molecule is a cross-linked polymer. Fragments released include D–D dimer or D_2 (two cross-linked D fragments) with a molecular weight of 160,000 daltons, D_2E, which is believed to be the principally released fragment *in vivo*, and

larger fragments containing combinations of both X and Y.

The anticoagulant effects of plasmin result not only from the destruction or inactivation of fibrin, fibrinogen, and other procoagulants, but also from the coagulation inhibiting properties of the fibrin(ogen) degradation products themselves. Fragments D and Y both inhibit coagulation in the clotting time test. Fragment X retains the ability to induce ADP-dependent platelet aggregation. Fragments Y, D, and E have lost the ability to induce and support platelet aggregation.

Activators of the Fibrinolytic System. There are several different pathways that lead to the activation of the plasminogen–plasmin proteolytic enzyme system. However, therapeutic (Fig. 4) utilization of this system occurs only by the exogenous administration of agents that initiate the conversion of inert plasminogen *[9001-91-6]* to the potent proteolytic enzyme plasmin *[9001-90-5]* (58). Currently, four thrombolytic agents have been approved for worldwide clinical use: streptokinase *[9002-01-1]* (SK) (59), urokinase *[9039-53-6]* (UK), recombinantly-produced tissue plasminogen activator (rTPA), and acylated Lysplasminogen–streptokinase activator complex (APSAC) (60,61). Some properties of these agents are listed in Table 7.

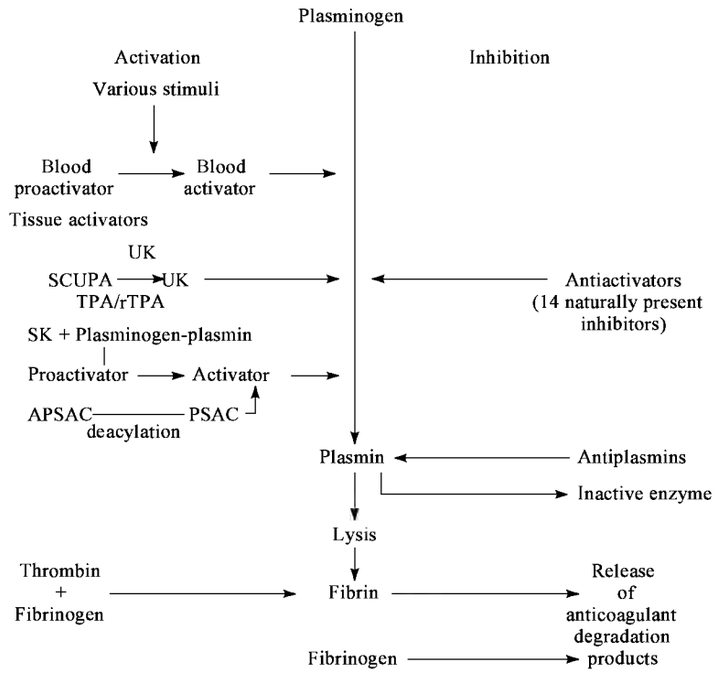


Fig. 4. Fibrinolytic system where SCUPA is single-chain urokinase plasminogen activator; rTPA is recombinant tissue plasminogen activator; APSAC is acylated plasminogen streptokinase activator complex; SK is streptokinase; and UK is urokinase.

Table 7. Properties of Approved Thrombolytic Agents

	SK[a]	UK[b]	rTPA[c]	APSAC[d]
source	*Streptococcal* culture	heterologous mammalian tissue culture	heterologous mammalian tissue culture	*Streptococcal* culture
mol wt, daltons	47,000	32,000–54,000	70,000	131,000
type of agent	bacterial proactivator	tissue plasminogen activator	tissue plasminogen activator	bacterial proactivator
plasma clearance, min	12–18	15–20	2–6	40–60
fibrinolytic activation	systemic	systemic	systemic	systemic
fibrin specificity	minimal	moderate	moderate	minimal
antigenic	yes	no	no	yes
allergic reactions	yes	no	no	yes
trade names	Streptase	Abbokinase	Alteplase (Activase)	Eminase
producer	Hoechst	Abbott Laboratories	Genentech Inc.	SmithKline Beecham Pharmaceuticals

[a] SK streptokinase.

[b] UK urokinase.

[c] rTPA = recombinant tissue plasminogen activator.

[d] APSAC acylated plasminogen streptokinase activator complex.

Additional agents that are known to activate the plasminogen system include single-chain urokinase plasminogen activator (SCUPA or pro-urokinase) and antibody directed thrombolytic agents, whereby an antibody is prepared against human fibrin and the Fab portion of this antibody coupled to SK, UK, and rTPA. All the known thrombolytic agents activate the fibrinolytic system by enzymatically inducing a clip at an arginine–valine amino acid sequence (560–561), which converts the single-chain plasminogen molecule to a two-chain structure, heavy and light chains, joined by a single disulfide bridge (58). Within the light-chain moiety an active serine center opens, and this is designated plasmin. Plasmin is a nonspecific proteolytic enzyme that has the capacity to degrade arginyl–lysyl bonds but kinetically, with respect to V_{max} and K_M, has its greatest affinity for fibrin.

Many pharmacological agents have been observed to increase fibrinolytic activity *in vivo,* presumably through stimulation of the release of endogenous plasma plasminogen activator(s). Epinephrine *[51-43-4]* (qv), nicotinic acid *[59-67-6]*, and vasopressin *[9034-50-8]* were some of the earlier substances discovered to have this action. Subsequently, other drugs that stimulate the release of epinephrine, eg, insulin, oral hypoglycemics, corticosteroids, and anabolic steroids, have also demonstrated an ability to enhance fibrinolytic activity. Unfortunately, in most cases the effect is transient and resistance develops after a few weeks of treatment. However, one of the anabolic steroids, Stanazol, has shown promise as a useful therapeutic agent (62).

Inhibitors of Fibrinolysis. Inhibitors of the fibrinolytic system are either endogenous naturally occurring inhibitors or modulators or

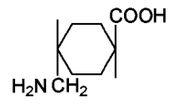
exogenous inhibitors employed primarily for therapeutic reasons.

The naturally occurring endogenous inhibitors modulators of *in vivo* activity of the plasminogen–plasmin proteolytic enzyme system have been considered and listed previously. Some of these inhibitors increase in concentration during certain physiologic states, ie, pregnancy when PAI-1 increases three to fourfold above normal and decreases the normal degree of fibrinolytic activity. In various pathologic conditions, several of these inhibitors are increased many fold above normal and exercise a paralytic effect on the fibrinolytic system.

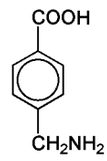
Several synthetic amino acids (63–65) have been identified that excite inhibition of the fibrinolytic system (Table 8).

$$H_2NCH_2(CH_2)_4COOH$$

(10)



(11)



(12)

Some of these agents prevent the conversion of plasminogen to plasmin whereas others block the degradative action of plasmin. A few of these agents inhibit both the conversion of plasminogen and hence the proteolytic action of plasmin, and the activity of the complement system. These agents experience wide use whenever there is a need to reduce the activity of the fibrinolytic system. In addition, these agents prevent excessive blood loss in patients with ulcerative colitis (66,67); menometrorrhagia; post-surgical prostatectomy (68); hereditary angioneurotic edema (69,70); oral surgery of any type, but in particular, dental extractions in patients with hemophilia A, hemophilia B, and von Willebrand disease (71); and immune and nonimmune-mediated thrombocytopenia (72). These antifibrinolytic agents inhibit complement activity and are often useful in immunologically-mediated phenomena such as asthma, post-organ transplantation, post-transfusion hemolysis (73), and neoplasia (74).

Table 8. Synthetic Therapeutic Fibrinolytic Inhibitors

Names	Trade name, company	CAS Registry Number	Dose
ε-aminocaproic acid, 6-aminohexanoic acid (10)	Amicar, Lederle	*[60-32-2]*	4–6 g loading dose followed by 1 g 2–4 h iv or oral
transexamic acid, *trans*-4-(aminomethyl)-cyclohexanecarboxylic acid (11)	Amstat, Lederle	*[1197-18-8]*	10 mg kg 3 times daily iv or 10–20 mg kg orally
aprotinin, trypsin inhibitor[a]	Trasylol, Delbay	*[9087-70-1]*	initial dose of 100,000 kIU[b] iv followed by 100,000 kIU iv h
p-aminomethylbenzoic acid (PAMBA) (12)		*[4389-45-1]*	not applicable for chemical use

[a] Protein, mol wt 6200.

[b] Kallikrein international units.

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BLOOD, FRACTIONATION.

See FRACTIONATION, BLOOD.

BLOWING AGENTS.

See FOAMED PLASTICS.

BLUE PRINTING.

See PRINTING PROCESSES.

BORDEAUX MIXTURE.

See FUNGICIDES, AGRICULTURAL.

BORON, ELEMENTAL

Boron *[7440-42-8]*, B, is unique in that it is the only nonmetal in Group 13 (IIIA) of the Periodic Table. Boron, at wt 10.81, at no. 5, has more similarity to carbon and silicon than to the other elements in Group 13. There are two stable boron isotopes, ^{10}B and ^{11}B, which are naturally present at 19.10–20.31% and 79.69–80.90%, respectively. The range of the isotopic abundancies reflects a variability in naturally occurring deposits such as high ^{10}B ore from Turkey and low ^{10}B ore from California. Other boron isotopes, ^{8}B, ^{12}B, and ^{13}B, have half-lives of less than a second. The ^{10}B isotope has a very high cross-section for absorption of thermal neutrons, 3.835×10^{-25} m^2 (3835 barns). This neutron absorption produces alpha particles.

There is a very low cosmic abundance of boron, but its occurrence at all is surprising for two reasons. First, boron's isotopes are not involved in a star's normal chain of thermonuclear reactions, and second, boron should not survive a star's extreme thermal condition. The formation of boron has been proposed to arise predominantly from cosmic ray bombardment of interstellar gas in a process called spallation (1).

Boron is the 51st most common element present in the earth's crust at a concentration of three grams per metric ton. A widespread boron mineral is tourmaline *[1317-93-7]*, a complex borosilicate of aluminum containing about 10% boron. However, the most common ores are alkali and alkaline-earth borates. Examples include borax *[1303-96-4]*, $Na_4B_4O_2 \cdot 10H_2O$, the most important ore of boron; kernite *[12045-87-3]*, $Na_2B_4O_7 \cdot 4H_2O$; colemanite *[1318-33-8]*, $Ca_2B\ O_{11} \cdot 5H_2O$; and ulexite *[1319-33-1]*, $NaCaB_5O_9 \cdot 8H_2O$. Commercial deposits are rare; the two principal ones are in the Mojave desert in California and in Turkey (see BORON COMPOUNDS, BORON OXIDES).

Properties

Elemental boron has a diverse and complex chemistry, primarily influenced by three circumstances. First, boron has a high ionization energy, 8.296 eV, 23.98 eV, and 37.75 eV for first, second, and third ionization potentials, respectively. Second, boron has a small size. Third, the electronegativities of boron (2.0), carbon (2.5), and hydrogen (2.1) are all very similar resulting in extensive and unusual covalent chemistry.

Boron has electronic structure $1s^2 2s^2 2p$ and an expected valence of three. Because of the high ionization energies there is no formation of univalent compounds as for the other Group 13 elements. Boron forms planar tricovalent compounds, BX_3, X halides, alkyls, etc, having the expected 120° bonding angles. The empty *p* orbital makes these compounds electron-pair acceptors or Lewis acids. Alkyls and halides of aluminum dimerize to make up for the deficiency of electrons, but the boron atom is too small to coordinate strongly.

Boron also has a high affinity for oxygen-forming borates, polyborates, borosilicates, peroxoborates, etc. Boron reacts with water at temperatures above 100°C to form boric acid and other boron compounds (qv).

Boron is electron deficient relative to carbon. Therefore, small amounts of boron, replacing carbon in a diamond lattice, causes electron holes. As electrons move to fill these lattice vacancies, infrared light is absorbed causing the blue color of the Hope diamond and other blue diamonds.

Boron forms B–N compounds that are isoelectronic with graphite (see BORON COMPOUNDS, REFRACTORY BORON COMPOUNDS). The small size also has a significant role in the interstitial alloy-type metal borides boron forms. Boron forms borides with metals that are less electronegative than itself including titanium, zirconium, and hafnium.

Boron's electron deficiency does not permit conventional two-electron bonds. Boron can form multicenter bonds. Thus the boron hydrides have structures quite unlike hydrocarbons. The ^{11}B nucleus, which has a spin of 3 2, which has been employed in boron nuclear magnetic resonance spectroscopy.

Crystalline boron is very inert. Low purity, higher temperatures, and changes in or lack of crystallinity all increase the chemical reactivity. Hot concentrated H_2SO_4–HNO_3 at 2:1 ratio can be used to dissolve boron for chemical analysis but boron is not soluble in boiling HF or HCl. Boron is also unreactive toward concentrated NaOH up to 500°C. At room temperature, boron reacts with F_2, but only superficially with O_2.

The physical properties of elemental boron are significantly affected by purity and crystal form. In addition to being an amorphous powder, boron has four crystalline forms: α-rhombohedral, β-rhombohedral, α-tetragonal, and β-tetragonal. The α-rhombohedral form has mp 2180°C, sublimes at approximately 3650°C, and has a density of 2.45 g mL. Amorphous boron, by comparison, has mp 2300°C, sublimes at approximately 2550°C, and has a density of 2.35 g mL.

Boron is an extremely hard refractory solid having a hardness of 9.3 on Mohs' scale and a very low (1.5×10^{-6} ohm^{-1} cm^{-1}) room temperature electrical conductivity so that boron is classified as a metalloid or semiconductor. These values are for the α-rhombohedral form.

The electron-deficient character of boron also affects its allotropic forms. The high ionization energies and small size prevent boron from adopting

metallic bonding to compensate for its electron deficiency and that of other hypoelectronic elements. The structural unit dominating boron's covalent bonding is the B_{12} icosahedron.

The α-rhombohedral form of boron has the simplest crystal structure with slightly deformed cubic close packing. At 1200°C α-rhombohedral boron degrades, and at 1500°C converts to β-rhombohedral boron, which is the most thermodynamically stable form. The unit cell has 104 boron atoms, a central B_{12} icosahedron, and 12 pentagonal pyramids of boron atom directed outward. Twenty additional boron atoms complete a complex coordination (2).

The α-tetragonal form of boron has a unit cell $B_{50}C_2$ or $B_{50}N_2$; it always has a carbon or nitrogen in the crystal. The cell is centered: a single-boron atom is coordinated to four icosahedrons ($4B_{12}$ + 2B). The β-tetragonal form has a unit cell of 192 boron atoms but is not, as of this writing, totally defined.

Preparation

Amorphous boron, discovered and named by Sir Humphry Davy in 1807, was first made by electrolyzing boric acid. Then in 1808, boron was produced by using potassium to reduce boric acid. The initial reactions resulted in boron that was less than 50% pure. A process to produce boron of over 90% purity was developed in 1892 by reducing boric oxide with magnesium, and by 1909, >99% boron was obtained by the decomposition of boron trichloride in hydrogen using an alternating current arc. These three methods, electrolytic reduction, chemical reduction, and thermal decomposition, are still used on a laboratory scale. A high purity (greater than 99%) boron comes from the direct thermal decomposition of boron hydrides such as diborane *[19287-45-7]*, B_2H . The kinetics of boron formation is discussed in an excellent review (3). Less pure boron from other methods can be purified by zone-refining (qv) or progressive recrystallization.

Production

The Moissan process, the reduction of boric oxide with magnesium, is the most widely used commercial process for producing boron. Although boric oxide can be reduced by many other agents, including calcium and potassium, the most efficient is magnesium. This process yields material from 90–92% pure. The boron is then leached with acid to separate it from the magnesium oxide formed in the process followed by multiple washes and final drying. Chemical processing can increase this purity to 95–97% pure. Boron is ground and made available in a particle size of about one micrometer. Multiple steps require an increase in handling of chemical waste, which must be recycled or disposed.

Another commercial process yields high purity boron of greater than 99%. In this process boron hydrides, such as diborane, are thermally decomposed (4). Because only boron and hydrogen are present in the starting material, contamination is minimal, and a very uniform, submicrometer powder is formed by the gas nucleation process.

Applications

Elemental boron is used in very diverse industries from metallurgy (qv) to electronics. Other areas of application include ceramics (qv), propulsion, pyrotechnics, and nuclear chemistry. Boron is nontoxic. Workplace hygienic practices, however, include avoiding the breathing of boron dust or fine powder.

Dispersed mixtures of boron and another metal are used as deoxidizing and degassing agents to harden steel (qv) (5,6), to increase the conductivity of copper (qv) in turbojet engines, and in the making of brass and bronze (see COPPER ALLOYS). Two examples are alloys of ferroboron and manganese boron.

Another metallurgical application is in amorphous magnetic alloys that are based on boron and iron, nickel, or cobalt (see MAGNETIC MATERIALS, BULK). The boron is used in power transformers as a soft magnet to convert from high to lower voltage; this material is commercially available from Allied-Signal, Inc. under the trademark METGLAS (see GLASSY METALS).

Another material that has permanent magnetic properties is neodymium–iron–boron, $Nd_2Fe_{14}B$. For an in-depth discussion see reference 7. Aimants Ugima, a member of the Pechiney Group, is a leading producer of rare-earth magnets in both the United States and Europe. Sumitomo Special Metals of Japan also produces these rare-earth magnets under the trade name of Neomax, and General Motors has commercial-scale production of a material called MAGNEQUENCH. The first World Solar Challenge Race, in 1987, was won using an electric motor fabricated using Nd–Fe–B. More mundane applications for cars include fuel pump motors, headlight door motors, starter motors, and heater motors. A patent has also been awarded for Nd–Fe–B bonded in polymer material that can be stamped and shaped easily for making electronic components for applications including stereo speakers and computer chip switches (8) (see MAGNETIC MATERIALS, THIN FILM).

The ceramic, polycrystalline silicon carbide *[409-21-2]*, SiC, is processed using β-silicon carbide and boron (9). The boron is a sintering aid used at 0.3–3% by weight to densify the sintered body to at least 85% of theoretical. The increased density improves strength (see ADVANCED CERAMICS; CERAMICS).

Boron filaments are formed by the chemical vapor deposition of boron trichloride on tungsten wire. High performance reinforcing boron fibers are available from 10–20 mm in diameter. These are used mainly in epoxy resins and aluminum and titanium. Commercial uses include golf club shafts, tennis and squash racquets, and fishing rods. The primary use is in the aerospace industry.

Boron has been studied as a possible fuel for solid fuel ramjets (10,11). Fine particle sized boron, where the average particle size is 0.3 μm, has been studied for use as a gas-generating agent for solid fuel ram rockets (12).

Boron mixed with an oxidizer is used as a pyrotechnic. This ordnance application for missiles and rockets is predominantly military. However, boron is also used in air bags, placed in automobiles as safety devices, for initiating the sodium azide *[26628-22-8]* which fills the bag with nitrogen (13). Other boron compounds are also used in the air-bag pyrotechnic application.

Boron creates an electron deficiency in the silicon lattice resulting in a *p*-type semiconductor for *p–n* junctions. Boron compounds are more commonly used as the dopant, however (see BORON HYDRIDES).

The high cross-section for thermal neutrons results in the use of boron and boron compounds for radiation shielding (14). The ease of detecting the α-particle produced when boron absorbs thermal neutrons results in the use of boron for neutron counters as well.

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BORON COMPOUNDS

Boron oxides, boric acid, and borates,
Boric acid esters,
Refractory boron compounds,
Boron halides,
Boron hydrides heteroboranes, and their metalla derivatives,
Commercial aspects,
Organic boron–nitrogen compounds,

BORON OXIDES, BORIC ACID, AND BORATES

The oxides and oxyacids of boron as well as a variety of hydrated and anhydrous metal borates are discussed herein. An alphabetical list of compounds referred to in the text is given in Table 1.

Table 1. Oxides and Borates Referred to in Text

Compound	CAS Registry Number	Molecular formula
ammonium pentaborate tetrahydrate	*[12229-12-8]*	$NH_4B_5O_8 \cdot 4H_2O$
barium metaborate hydrate	*[13701-59-2]*	$BaO \cdot B_2O_3 \cdot xH_2O$
boron dioxide	*[13840-88-5]*	BO_2
boron monoxide	*[12505-77-0]*	BO
boron oxide (6:1)	*[11056-99-8]*	B_6O
boron oxide (7:1)	*[12447-73-3]*	B_7O
boron oxide (13:2)	*[56940-67-1]*	$B_{13}O_2$
boron phosphate	*[13308-51-5]*	BPO_4
boron suboxide	*[54723-68-1]*	$B_{12}O_2$
boron oxide (12:2)	*[54723-68-1]*	$B_{12}O_2$
diammonium tetraborate tetrahydrate	*[12228-87-4]*	$(NH_4)_2O \cdot 2B_2O_3 \cdot 4H_2O$
diboron dioxide	*[13766-28-4]*	B_2O_2
boron oxide (2:2)	*[13766-28-4]*	B_2O_2
diboron trioxide	*[1303-86-2]*	B_2O_3
boron oxide (2:3)	*[1303-86-2]*	B_2O_3
dicalcium hexaborate pentahydrate	*[12291-65-5]*	$2CaO \cdot 3B_2O_3 \cdot 5H_2O$
dipotassium tetraborate tetrahydrate	*[12045-78-2]*	$K_2O \cdot 2B_2O_3 \cdot 4H_2O$
disodium octaborate tetrahydrate	*[12280-03-4]*	$Na_2O \cdot 4B_2O_3 \cdot 4H_2O$
disodium tetraborate	*[1330-43-4]*	$Na_2O \cdot 2B_2O_3$
disodium tetraborate decahydrate (borax)	*[1303-96-4]*	$Na_2O \cdot 2B_2O_3 \cdot 10H_2O$
disodium tetraborate pentahydrate	*[12045-88-4]*	$Na_2O \cdot 2B_2O_3 \cdot 5H_2O$
disodium tetraborate tetrahydrate	*[12045-87-3]*	$Na_2O \cdot 2B_2O_3 \cdot 4H_2O$
dizinc hexaborate heptahydrate	*[12280-01-2]*	$Zn_2B_6O_{11} \cdot 7H_2O$
metaboric acid	*[13460-50-9]*	HBO_2
orthoboric acid	*[10043-35-3]*	$B(OH)_3$
potassium pentaborate tetrahydrate	*[12229-13-9]*	$KB_5O_8 \cdot 4H_2O$
sodium calcium pentaborate octahydrate	*[1319-33-1]*	$NaCaB_5O_9 \cdot 8H_2O$
sodium calcium pentaborate pentahydrate	*[12229-14-0]*	$NaCaB_5O_9 \cdot 5H_2O$
sodium metaborate dihydrate	*[16800-11-6]*	$NaBO_2 \cdot 2H_2O$
sodium metaborate tetrahydrate	*[10555-76-7]*	$NaBO_2 \cdot 4H_2O$
sodium pentaborate pentahydrate	*[12046-75-2]*	$NaB_5O_8 \cdot 5H_2O$
sodium perborate tetrahydrate	*[10486-00-7]*	$NaBO_3 \cdot 4H_2O$
sodium perborate trihydrate	*[28962-65-4]*	$NaBO_3 \cdot 3H_2O$
sodium perborate monohydrate	*[10332-33-9]*	$NaBO_3 \cdot H_2O$
zinc salt (1:2), hydrate	*[12447-61-9]*	$2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$
zinc diborate dihydrate	*[27043-84-1]*	$ZnO \cdot B_2O_3 \cdot 2H_2O$
zinc triborate monohydrate	*[12429-73-1]*	$Zn(B_3O_3(OH)_5) \cdot H_2O$

The confusing and often ambiguous systems of nomenclature encountered in the literature of inorganic borates have been described (1). The accumulation of detailed structural data for many of the crystalline compounds has led to derivation of more complex names and formulas in an effort to convey more precise information; *Chemical Abstracts* has adopted a classification system based on a series of the usually hypothetical boric acids. For example, the compound having empirical formula $Zn_2B_6O_{11} \cdot 7H_2O$ has been called dizinc hexaborate heptahydrate. Applying the resolved oxide system proposed by the IUPAC, the substance becomes $2ZnO \cdot 3B_2O_3 \cdot 7H_2O$, known as zinc (2:3) borate heptahydrate. This latter system has gained wide acceptance and is followed herein. However, knowledge of the crystal structure allows a more precise structural formulation, $Zn(B_3O_3(OH)_5) \cdot H_2O$, ie, zinc triborate monohydrate, which is listed in *Chemical Abstracts* as boric acid, $H_7B_3O_8$, zinc salt *[12429-73-1]* (2). Because many authors continue to use the older formulations, a second listing has been devised by *Chemical Abstracts* for the same compound, ie, boric acid, $H_4B_6O_{11}$, zinc salt (1:2) heptahydrate *[12280-01-2]*.

Borate Minerals

The principal borate minerals are listed in Table 2. A much more complete listing is available in the literature (3,4). Crystal structures of known borate compounds have been compiled (5).

Table 2. Borate Minerals

Mineral	CAS Registry Number	Composition formula	B_2O_3, wt %
sassolite	[10043-35-3]	$B(OH)_3$	56.3
borax (tincal)	[1303-96-4]	$Na_2O \cdot 2B_2O_3 \cdot 10H_2O$	36.5
tincalconite	[12045-88-4]	$Na_2O \cdot 2B_2O_3 \cdot 4.67H_2O$	48.8
kernite	[12045-87-3]	$Na_2O \cdot 2B_2O_3 \cdot 4H_2O$	50.9
inyoite	[12260-25-2]	$2CaO \cdot 3B_2O_3 \cdot 13H_2O$	37.6
meyerhofferite	[57572-66-4]	$2CaO \cdot 3B_2O_3 \cdot 7H_2O$	46.7
colemanite	[12291-65-5]	$2CaO \cdot 3B_2O_3 \cdot 5H_2O$	50.8
priceite (pandermite)	[61583-61-7]	$4CaO \cdot 5B_2O_3 \cdot 7H_2O$	49.8
ulexite	[1319-33-1]	$Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 16H_2O$	43.0
probertite	[12229-14-0]	$Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 10H_2O$	49.6
hydroboracite	[12046-12-7]	$CaO \cdot MgO \cdot 3B_2O_3 \cdot 6H_2O$	50.5
inderite	[12260-26-3]	$2MgO \cdot 3B_2O_3 \cdot 15H_2O$	37.3
szaibelyite (asharite)[a]	[12447-04-0] [36564-04-2]	$2MgO \cdot B_2O_3 \cdot H_2O$	41.4
datolite	[1318-40-7]	$2CaO \cdot B_2O_3 \cdot 2SiO_2 \cdot H_2O$	21.8
howlite	[1318-68-9]	$4CaO \cdot 5B_2O_3 \cdot 2SiO_2 \cdot 5H_2O$	44.4

[a] This material has two CAS Registry Numbers.

Borax (tincal), kernite, colemanite, ulexite, probertite, hydroboracite, inderite, datolite, and szaibelyite (ascharite) are the only borate minerals of commercial importance. Borax and colemanite are the most important. Borate production comes mostly from seven countries: the United States, Turkey, Russia, Kazakhstan, Argentina, China, Peru, and Chile. Deposit areas and reserves in these countries are shown in Table 3.

Table 3. Distribution of Borate Minerals

Country	Area	Principal minerals	Reserves, 10^6 t of B_2O_3
United States	Boron, Calif.	tincal, kernite	41–50
	Searles Lake, Calif.	brine	15
	Death Valley, Calif.	colemanite, ulexite, probertite	several
Turkey	Bigadic	colemanite, priceite, ulexite	
	Emet	colemanite	23
	Kirka	tincal, colemanite, ulexite	122
Kazakhstan	Inder	szaibelyite	54
Russia	Dal'negorsk	datolite	
Argentina	Tincalayu	tincal, kernite, ulexite	23
China	Liaoning	szaibelyite	27

Reports have been made concerning the minerals of the Searles Lake (7), the Boron-Kramer (8), and the Death Valley (7) areas in the United States. The mineralogy of the Kirka (9) and Emet (10) districts of Turkey have been described. A number of general reviews give information on borate manufacture, economics and mineralogy (11,12) and a review on boron geochemistry has been compiled (13). The application of crystallographic data to borate geology has been described (14), and the history of borate mining and production in the United States (15) and in the world (16) has been reviewed.

Boron Oxides

Boric Oxide. Boric oxide, B_2O_3, formula wt 69.62, is the only commercially important oxide. It is also known as diboron trioxide, boric anhydride, or anhydrous boric acid. B_2O_3 is normally encountered in the vitreous state. This colorless, glassy solid has a Mohs' hardness of 4 and is usually prepared by dehydration of boric acid at elevated temperatures. It is mildly hygroscopic at room temperature, and the commercially available material contains ca 1 wt % moisture as a surface layer of boric acid. The reaction with water:

$$B_2O_3\ (\text{glass}) + 3\ H_2O \rightarrow 2\ B(OH)_3$$

is exothermic, ΔH° 75.94 kJ/mol (−18.15 kcal/mol) B_2O_3 (17).

Boric oxide is an excellent Lewis acid. It coordinates even weak bases to form four-coordinate borate species. Reaction with sulfuric acid produces $H[B(HSO_4)_4]$ (18). At high (>1000°C) temperatures molten boric oxide dissolves most metal oxides and is thus very corrosive to metals in the presence of oxygen.

Molten boric oxide reacts readily with water vapor above 1000°C to form metaboric acid in the vapor state.

$$B_2O_3\ (\text{glass}) + H_2O(g) \rightarrow 2\ HBO_2(g)$$

A value of ΔH_{298} 199.2 ± 8.4 kJ/mol (47.61 ± 2.0 kcal/mol) has been calculated for this reaction, which is of considerable economic importance to glass manufacturers because B_2O_3 losses during glass (qv) processing are greatly increased by the presence of water. For this reason anhydrous borates or boric oxide are often preferred over hydrated salts, eg, borax or boric acid for glass manufacture. The presence of MgO has been found to reduce volatilization of B_2O_3 from glass charges (19).

The physical properties of vitreous boric oxide (Table 4) are somewhat dependent on moisture content and thermal history. Much of the older physical data has been revised following development of more reliable techniques for sample preparation (23,24). Many physical properties are sensitive to moisture present as metaboric acid, not as free water. Water can be reduced to 0.17% by heating in air at 1000°C and a level of 10 ppm has been achieved by prolonged heating in a vacuum, 0.13 kPa (1 mm Hg), in a carbon crucible. Removal of residual water causes the density to decrease and softening point at 6×10^6 Pa·s (6×10^7 P) to increase. At 0.28 wt % of water the density of boric oxide is 1.853, softening point 240–275°C; nearly anhydrous B_2O_3, having 20 ppm water has density of 1.829 g/mL and a softening point of 300–325°C (25). Thermal expansion, viscosity, and refractive index are all affected by moisture content. Boric oxide becomes pourable on heating to about 500°C. The viscosity of boric oxide with temperature is given below.

Temperature, °C	Viscosity, Pa·s	Temperature, °C	Viscosity, Pa·s
260	6.1×10^{10}	700	8.5×10
300	4.4×10^{8}	800	2.6×10
400	1.6×10^{5}	900	1.2×10
500	3.9×10^{3}	1000	7.4
600	4.8×10^{2}	1100	4.3

Table 4. Physical Properties of Vitreous Boric Oxide

Property	Value	Reference
vapor pressure[a], 1331–1808 K	$\log P = 5.849 - \frac{16960}{T}$	20
heat of vaporization, ΔH_{vap}, kJ/mol[b]		
1500 K	390.4	21
298 K	431.4	21
boiling point, extrapolated	2316°C	17
viscosity, log η, mPa·s (=cP)		
350°C	10.60	22
700°C	4.96	22
1000°C	4.00	22
density, g/mL		
0°C	1.8766	
18–25°C	1.844	
18–25°C[c]	1.81	
500°C[d]	1.648	22
1000°C[d]	1.528	22
index of refraction, 14.4°C	1.463	
heat capacity (specific), J/(kg·K)[b]		
298 K	62.969	17
500 K	87.027	17
700 K	132.63	17
1000 K	131.38	17
heat of formation[e], ΔH_f, kJ/mol[b], 298.15 K	-1252.2 ± 1.7	17

[a] P is in units of kPa; T is in K. To convert kPa to torr, multiply by 7.5.

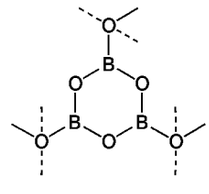
[b] To convert J to cal, divide by 4.184.

[c] Well-annealed.

[d] Quenched.

[e] For $2\,B(s) + \frac{3}{2}O_2(g) \rightarrow B_2O_3$ (glass).

The historical debate over the molecular structure of vitreous and molten boric oxide may never be completely resolved because of its amorphous nature (26). There are only trigonal borons in the solid glass and these are believed to have a branched network of planar boroxol $(-BO-)_3$ rings (1). The three exocyclic oxygens, outside the ring, form bridges to neighboring rings or to planar BO_3 groups (27,28). This network breaks down as the glass melts, and spectroscopic features attributed to the boroxol group, eg, the strong Raman line at 808 cm^{-1}, decrease as the liquid is heated to 800°C. It has been proposed (24) that above 800°C the liquid consists of discrete, but strongly associated, small molecules, conceivably the same monomeric B_2O_3 units observed in the vapor state (29).



(1)

Two crystalline forms of boric oxide have been prepared, and the structures of both materials have been determined by x-ray diffraction (18). The phase relationships between the liquid and crystalline forms have also been developed (30). The more common hexagonal crystal phase, B_2O_3-I or α-form (d = 2.46 g/mL, mp = 455–475°C), is more stable than the vitreous phase. The effect of residual water in crystalline B_2O_3, as in the vitreous phase, is to lower the melting, softening, and freezing points (31). For the transformation $B_2O_3\text{-I} \rightarrow B_2O_3$ (glass), $\Delta H° = +18.24$ kJ/mol (4.36 kcal/mol) (17). However, vitreous B_2O_3 does not crystallize in the absence of seed crystals or increased pressure. Crystallization of B_2O_3 can be induced by prolonged heating of melt with <18 wt % water below 235°C or in the presence of 5 wt % water and addition of crystalline B_2O_3 seed at 250°C. Crystals do not form at any temperature from melt containing <1 wt % water. Crystalline B_2O_3 can also be made by prolonged heating of boric acid seeded with boron phosphate at 220 to 260°C (32). A second dense monoclinic crystalline phase, B_2O_3-II or β-form (d = 2.95 g/mL, mp = 510°C) can be obtained at 400°C and >2.23 GPa (>22,000 atm). The crystal lattice of B_2O_3-II consists of a highly compact network of BO_4 tetrahedra where the four apical oxygens are shared by either two or three boron atoms. The acidic character associated with trigonal BO_3 groups is thus masked in B_2O_3-II. Although this material is thermodynamically unstable under ordinary conditions, it reacts very slowly with Lewis bases such as water and fluoride ion.

In the United States a high (99% B_2O_3) purity grade is produced by fusing refined, granular boric acid in a glass furnace fired by oil or gas. The molten glass is solidified in a continuous ribbon as the melt flows over chill-rolls. The amorphous solid product is crushed, screened, and packed in sacks or drums with moisture-proof liners. The price of this product has increased 11% since the mid-1980s and more than doubled since 1977. The carload (>36 metric tons) price in January 1990 was \$2780–2950/t (fob plant) depending on mesh size and packaging (33). Boric oxide is no longer commercially

produced by mixing borax and sulfuric acid in a fusion furnace. There is no commercial source of crystalline boric oxide (B_2O_3).

Boric oxide reacts with water to form boric acid, with halogens to form boron trihalides, with halogen salts to form glasses, and with P_2O_5 to form boron phosphate. It also is a powerful Lewis acid solvent for dissolving metal oxides, has a low surface tension, and readily wets metal surfaces. Boric oxide can be used as a solvent for metal reductions such as $2\ CuO + C \rightarrow CO_2 + 2\ Cu$, for growing crystals of garnet, refractory oxides, and preparation of lead titanate, barium titanate, and calcium zirconates from the corresponding oxides.

The uses of boric oxide relate to its behavior as a flux, an acid catalyst, or a chemical intermediate. The fluxing action of B_2O_3 is important in preparing many types of glass, glazes, frits, ceramic coatings, and porcelain enamels (qv).

Boric oxide is used as a catalyst in many organic reactions. It also serves as an intermediate in the production of boron halides, esters, carbide, nitride, and metallic borides.

Boron Monoxide and Dioxide. High temperature vapor phases of BO, B_2O_3, and BO_2 have been the subject of a number of spectroscopic and mass spectrometric studies aimed at developing theories of bonding, electronic structures, and thermochemical data (1,34). Values for the principal thermodynamic functions have been calculated and compiled for these gases (35).

Vibrational emission spectra indicate that the B_2O_2 molecule has a linear O═B—B═O structure. Values of 782 and 502 kJ mol (187 and 120 kcal mol) were calculated for the respective B═O and B—B bond energies (36).

Two noncrystalline solid forms of BO have been prepared (1,34). Several polymeric $(BO)_n$ or $(B_2O_2)_n$ structures have been proposed for these materials. Although conclusive structural evidence is unavailable, the presence of B—B bonds appears likely. The low temperature form is a white, water-soluble powder produced at 220°C by vacuum-dehydration of tetrahydroxydiborane(4), *[13675-18-8]* $B_2(OH)_4$, that can be prepared from tetrakis(dimethylamino)diborane(4) *[1630-79-1]* (37). This product is irreversibly converted to an insoluble, light brown modification on heating above 500°C. The latter material was also prepared by reduction of B_2O_3 by boron at 1330°C, by carbon, or by boron carbides at 1250°C (38). Both BO polymorphs are strong reducing agents that decompose slowly in water to yield hydrogen gas and boric acid.

$$B_2O_3 + C \rightarrow B_2O_2 + CO$$

$$5\ B_2O_3 + B_4C \rightarrow 7\ B_2O_2 + CO$$

Lower Oxides. A number of hard, refractory suboxides have been prepared either as by-products of elemental boron production (1) or by the reaction of boron and boric acid at high temperatures and pressures (39). It appears that the various oxides represented as B O, B_7O, $B_{12}O_2$, and $B_{13}O_2$ may all be the same material in varying degrees of purity. A representative crystalline substance was determined to be rhombohedral boron suboxide, $B_{12}O_2$, usually mixed with traces of boron or B_2O_3 (39). A study has been made of the mechanical properties of this material, which exhibits a hardness comparable to that of boron carbide (40). At temperatures above 1000°C, $B_{12}O_2$ gradually decomposes to B(s) and B_2O_2(g).

Boric Acid

The name boric acid is usually associated with orthoboric acid, which is the only commercially important form of boric acid and is found in nature as the mineral sassolite. Three crystalline modifications of metaboric acid also exist. All these forms of boric acid can be regarded as hydrates of boric oxide and formulated as $B_2O_3 \cdot 3H_2O$ for orthoboric acid and $B_2O_3 \cdot H_2O$ for metaboric acid.

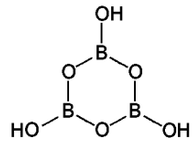
Forms of Boric Acid. Orthoboric acid, $B(OH)_3$, formula wt, 61.83, crystallizes from aqueous solutions as white, waxy plates that are triclinic in nature; sp gr^{14}_4, 1.5172. Its normal melting point is 170.9°C, however, when heated slowly it loses water to form metaboric acid, HBO_2, formula wt, 43.82, which may exist in one of three crystal modifications. Orthorhombic HBO_2-III or α-form (*d* 1.784 g mL, mp 176°C) forms first around 130°C and gradually changes to monoclinic HBO_2-II or β-form (*d* 2.045 g mL, mp 200.9°C). Water-vapor pressures associated with these decompositions follow. To convert kPa to mm Hg, multiply by 7.5.

Temperature, °C	Vapor pressure of H_2O over $B(OH)_3$ and HBO_2-III, kPa	and HBO_2-II, kPa
25	0.048	0.16
100	8.4	16
130	39.9	62.5
150	102	143

At temperatures above 150°C, dehydration continues to yield viscous liquid phases beyond the metaboric acid composition (39). The most stable form of metaboric acid, cubic HBO_2-I or γ-form (*d* 2.49 g mL, mp 236°C) crystallizes slowly when mixtures of boric acid and HBO_2-III are melted in an evacuated, sealed ampul and held at 180°C for several weeks (41).

The relationships between condensed phases in the B_2O_3–H_2O system are shown in Figure 1 (42). There is no evidence for stable phases other than those shown. B_2O_3 melts and glasses containing less than 50 mol % water have mechanical and spectroscopic properties consistent with mixtures of HBO_2 and vitreous B_2O_3.

Vapor phases in the B_2O_3 system include water vapor and $B(OH)_3$(g) at temperatures below 160°C. Appreciable losses of boric acid occur when aqueous solutions are concentrated by boiling (43). At high (600–1000°C) temperatures, HBO_2(g) is the principal boron species formed by equilibration of water vapor and molten B_2O_3 (44). At still higher temperatures a trimer $(HBO_2)_3$(g) (2) is formed.



(2)

The crystal structure of orthoboric acid consists of planar sheets made up of hydrogen-bonded, triangular $B(OH)_3$ molecules. The stacking pattern of the molecular layers is completely disordered, indicative of relatively weak van der Waals forces between the planes. This accounts for its slippery feel and the ease with which the crystals are cleaved into thin flakes (45). The structures of all three forms of metaboric acid are also known (46). The basic structural unit of HBO_2-III is the trimeric ring (2) and consists of only planar trigonal BO_3 units. Metaborate-I has only tetrahedral BO_4 structural units and HBO_2-II contains both trigonal and tetrahedral borons in a ratio of 2:1. The HBO_2-III trimer may persist to some extent in the vapor phase, but infrared spectra indicate that monomeric O═B—OH species predominate in gaseous metaboric acid (47).

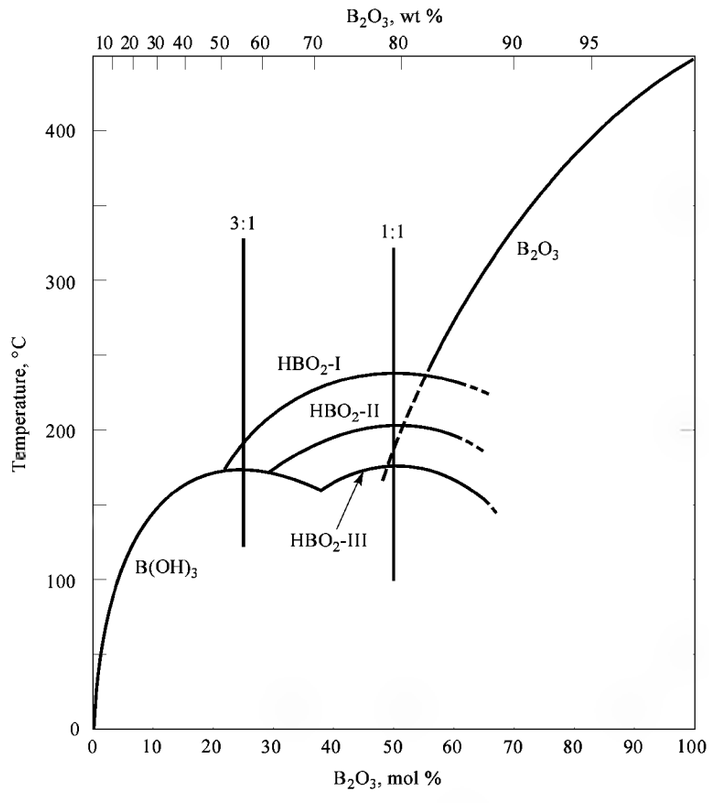


Fig. 1. Solubility diagram for the system H_2O–B_2O_3 (42).

Courtesy of The American Journal of Science.

Properties. The standard heats of formation of crystalline orthoboric acid and the three forms of metaboric acid are ΔH_f° 1094.3 kJ mol (261.54 kcal mol) for $B(OH)_3$; 804.04 kJ mol (192.17 kcal mol) for HBO_2-I; 794.25 kJ mol (189.83 kcal mol) for HBO_2-II; and 788.77 kcal mol (188.52 kcal mol) for HBO_2-III (48). Values for the principal thermodynamic functions of $B(OH)_3$ are given in Table 5 (17).

Table 5. Thermodynamic Properties of Crystalline Boric Acid, $B(OH)_3$[a]

Temperature, K	C°_p, J (kg·K)[b]	S°, J K[b]	$H^\circ - H^\circ_{298}$, J mol[b]
0	0	0	13393
100	35.92	28.98	11636
200	58.74	61.13	6866
298	81.34	88.74	0
400	100.21	115.39	9284

[a] Ref. 44.

[b] To convert J to cal, divide by 4.184.

The solubility of boric acid in water (Table 6) increases rapidly with temperature. The heat of solution is somewhat concentration dependent. For solutions having molalities in the range 0.03–0.9 *m*, the molar heats of solution fit the empirical relation (49):

$$\Delta H \quad [22062 \quad 222\, m + 979\, e^{\quad 1230\, m}] \text{ kJ mol}$$

The presence of inorganic salts may enhance or depress the aqueous solubility of boric acid: it is increased by potassium chloride as well as by potassium or sodium sulfate but decreased by lithium and sodium chlorides. Basic anions and other nucleophiles, notably borates and fluoride, greatly increase boric acid solubility by forming polyions (44).

Table 6. Aqueous Solubility of Boric Acid

Temperature, °C	$B(OH)_3$, wt %	Temperature, °C	$B(OH)_3$, wt %
0.76[a]	2.47	60	12.97
0	2.52	70	15.75
10	3.49	80	19.10
20	4.72	90	23.27
30	6.23	100	27.53
40	8.08	103.3[b]	29.27
50	10.27		

[a] Melting point.

[b] Boiling point.

Boric acid is quite soluble in many organic solvents (Table 7). Some of these solvents, eg, pyridine, dioxane, and diols, are known to form boric acid

complexes.

Table 7. Solubility of Boric Acid, Borax Decahydrate, and Borax Pentahydrate in Organic Solvents

Solvent	Temperature, °C	Solubility, wt %		
		$B(OH)_3$	$Na_2B_4O_7 \cdot 10H_2O$	$Na_2B_4O_7 \cdot 5H_2O$
glycerol, 86.5%	20	21.1	47.1	
glycerol, 98.5%	20	19.9	52.6	
glycerol	25	17.5		
ethylene glycol	25	18.5	41.6	31.2
propylene glycol	25	15.1		21.9
diethylene glycol	25	13.6	18.6	10.0
mannitol, 10%	25	6.62		
methanol	25	173.9[a]	19.9	16.9
ethanol	25	94.4[a]		
n-propanol	25	59.4[a]		
n-butanol	25	42.8[a]		
2-methylbutanol	25	35.3[a]		
isoamyl alcohol	25	2.39		
acetone	25	0.6	0.60	
methyl ethyl ketone	20	0.7		
ethyl acetate	25	1.5	0.14	
diethyl ether	20	0.008		
dioxane	25	ca 14.6[a]		
pyridine	25	ca 70[a]		
aniline	20	0.15		
acetic acid, 100%	30	6.3		

[a] Solubility values are in g L.

Dilute aqueous solutions of boric acid contain predominantly monomeric, undissociated $B(OH)_3$ molecules. The acidic properties of boric acid relate to behavior as a base acceptor, ie, as a Lewis acid, rather than as a proton donor. For the reaction

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$$

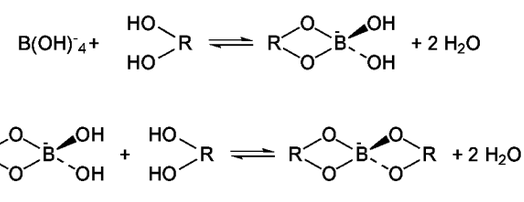
an equilibrium constant of 5.80×10^{-10} at 25°C has been reported (50). However, calculated pH values based on this constant deviate considerably from measured ones as the boric acid concentration is increased, as shown in Table 8. The increased acidity has been attributed to secondary equilibria involving condensation reactions between $B(OH)_3$ and $B(OH)_4^-$, tetrahydroxyborate *[15390-83-7]*, to produce polyborates. A trimeric species $B_3O_3(OH)_4^-$ *[17927-69-4]* appears to be the most important of these complex ions (52).

Table 8. Observed and Calculated pH Values for Boric Acid[a]

Concentration, *M*	pH observed	pH calculated
0.0603	5.23	5.23
0.0904	5.14	5.14
0.1205	5.01	5.08
0.211	4.71	4.96
0.422	4.22	4.80
0.512	4.06	4.76
0.753	3.69	4.54

[a] Ref. 51.

The apparent acid strength of boric acid is increased both by strong electrolytes that modify the structure and activity of the solvent water and by reagents that form complexes with $B(OH)_4^-$ and or polyborate anions. More than one mechanism may be operative when salts of metal ions are involved. In the presence of excess calcium chloride the strength of boric acid becomes comparable to that of carboxylic acids, and such solutions may be titrated using strong base to a sharp phenolphthalein end point. Normally titrations of boric acid are carried out following addition of mannitol or sorbitol, which form stable chelate complexes with $B(OH)_4^-$ in a manner typical of polyhydroxy compounds. Equilibria of the type:



have been exploited in other applications besides analytical determinations of boric acid (53). Ion-exchange resins containing polyols have been developed that are highly specific for removing borates from solution (54). A number of aliphatic and aromatic diols have been patented as extractants for borates and boric acid (55).

Boric acid and fluoride ion react to form a series of fluroborates where OH^- is displaced by F^-; (see FLUORINE COMPOUNDS, INORGANIC—BORON, FLUOROBORIC ACID). Stepwise formation of the ions fluorotrihydroxyborate *[32554-53-3]*, $BF(OH)_3^-$, difluorodihydroxyborate *[32554-52-2]*, $BF_2(OH)_2^-$, and trifluorotrihydroxyborate *[18953-00-9]*, $BF_3(OH)^-$, proceeds rapidly in acidic solutions, but tetrafluoroborate *[14874-70-5]*, BF_4^-, forms slowly (56). A fluorosubstituted polyborate, $B_3O_3F_3^-$ *[59753-06-9]*, has also been identified (52).

Alcohols react with boric acid with elimination of water to form borate esters, $B(OR)_3$. A wide variety of borate salts and complexes have been prepared by the reaction of boric acid and inorganic bases, amines, and heavy-metal cations or oxyanions (44,45). Fusion with metal oxides yields

anhydrous borates or borate glasses.

Manufacture. The majority of boric acid is produced by the reaction of inorganic borates with sulfuric acid in an aqueous medium. Sodium borates are the principal raw material in the United States. European manufacturers have generally used partially refined calcium borates, mainly colemanite from Turkey. Turkey uses both colemanite and tincal to make boric acid.

When granulated borax or borax-containing liquors are treated with sulfuric acid, the following reaction ensues:

$$Na_2B_4O_7 \cdot xH_2O + H_2SO_4 \rightarrow 4\,B(OH)_3 + Na_2SO_4 + (x - 5)\,H_2O$$

In the United States boric acid is produced by United States Borax & Chemical Corp. in a 103,000 B_2O_3 metric ton per year plant by reacting crushed kernite ore with sulfuric acid. Coarse gangue is removed in rake classifiers and fine gangue is removed in thickeners. Boric acid is crystallized from strong liquor, nearly saturated in sodium sulfate, in continuous evaporative crystallizers, and the crystals are washed in a multistage countercurrent wash circuit.

When boric acid is made from colemanite, the ore is ground to a fine powder and stirred vigorously with diluted mother liquor and sulfuric acid at about 90°C. The by-product calcium sulfate *[7778-18-9]* is removed by settling and filtration, and the boric acid is crystallized by cooling the filtrate.

A unique liquid–liquid extraction process for manufacturing boric acid from sodium borate brines has been operated at Searles Lake, Trona, California, by the North American Chemical Co. since 1962. Both potassium sulfate and sodium sulfate are produced as coproducts in this process.

Boric acid crystals are usually separated from aqueous slurries by centrifugation and dried in rotary driers heated indirectly by warm air. To avoid overdrying, the product temperature should not exceed 50°C. Powdered and impalpable boric acid are produced by milling the crystalline material.

The principal impurities in technical-grade boric acid are the by-product sulfates, <0.1 wt %, and various minor metallic impurities present in the borate ores. A boric acid titer is not an effective measure of purity because overdrying may result in partial conversion to metaboric acid and lead to $B(OH)_3$ assays above 100%. High purity boric acid is prepared by recrystallization of technical-grade material.

Three grades of granular and powdered boric acid are manufactured in the United States. In July 1990, carload (ca 91 metric ton) prices per metric ton of granular boric acid were: technical-grade, $805; NF-grade, $1562; and special quality-grade, $1892. All prices are fob plant for material packed in 45.4-kg multiwall sacks (33).

Uses. Boric acid has a surprising variety of applications in both industrial and consumer products (6,57). It serves as a source of B_2O_3 in many fused products, including textile fiber glass, optical and sealing glasses, heat-resistant borosilicate glass, ceramic glazes, and porcelain enamels (see ENAMELS, PORCELAIN AND VITREOUS). It also serves as a component of fluxes for welding and brazing (see SOLDERS AND BRAZING ALLOYS; WELDING).

A number of boron chemicals are prepared directly from boric acid. These include synthetic inorganic borate salts, boron phosphate, fluoborates, boron trihalides, borate esters, boron carbide, and metal alloys such as ferroboron *[11108-67-1]*.

Boric acid catalyzes the air oxidation of hydrocarbons and increases the yield of alcohols by forming esters that prevent further oxidation of hydroxyl groups to ketones and carboxylic acids (see HYDROCARBON OXIDATION).

The bacteriostatic and fungicidal properties of boric acid have led to its use as a preservative in natural products such as lumber, rubber latex emulsions, leather, and starch products.

NF-grade boric acid serves as a mild, nonirritating antiseptic in mouthwashes, hair rinse, talcum powder, eyewashes, and protective ointments (see DISINFECTANTS). Although relatively nontoxic to mammals (58), boric acid powders are quite poisonous to some insects. With the addition of an anticaking agent, they have been used to control cockroaches and to protect wood against insect damage (see INSECT CONTROL TECHNOLOGY).

Inorganic boron compounds are generally good fire retardants (59). Boric acid, alone or in mixtures with sodium borates, is particularly effective in reducing the flammability of cellulosic materials. Applications include treatment of wood products, cellulose insulation, and cotton batting used in mattresses (see FLAME RETARDANTS).

Because boron compounds are good absorbers of thermal neutrons, owing to isotope ^{10}B, the nuclear industry has developed many applications. High purity boric acid is added to the cooling water used in high pressure water reactors (see NUCLEAR REACTORS).

Solutions of Boric Acid and Borates

Polyborates and pH Behavior. Whereas boric acid is essentially monomeric in dilute aqueous solutions, polymeric species may form at concentrations above 0.1 *M*. The conjugate base of boric acid in aqueous systems is the tetrahydroxyborate *[15390-83-7]* anion sometimes called the metaborate anion, $B(OH)_4^-$. This species is also the principal anion in solutions of alkali metal (1:1) borates such as sodium metaborate, $Na_2O \cdot B_2O_3 \cdot 4H_2O$ (60). Mixtures of $B(OH)_3$ and $B(OH)_4^-$ appear to form classical buffer systems where the solution pH is governed primarily by the acid:salt ratio, ie, $[H^+] = K_a[B(OH)_3]/[B(OH)_4^-]$. This relationship is nearly correct for solutions of sodium or potassium (1:2) borates, eg, borax, where the ratio $B(OH)_3$:$B(OH)_4^-$ = 1, and the pH remains near 9 over a wide range of concentrations. However, for solutions that have pH values much greater or less than 9, the pH changes greatly on dilution as shown in Figure 2 (61).

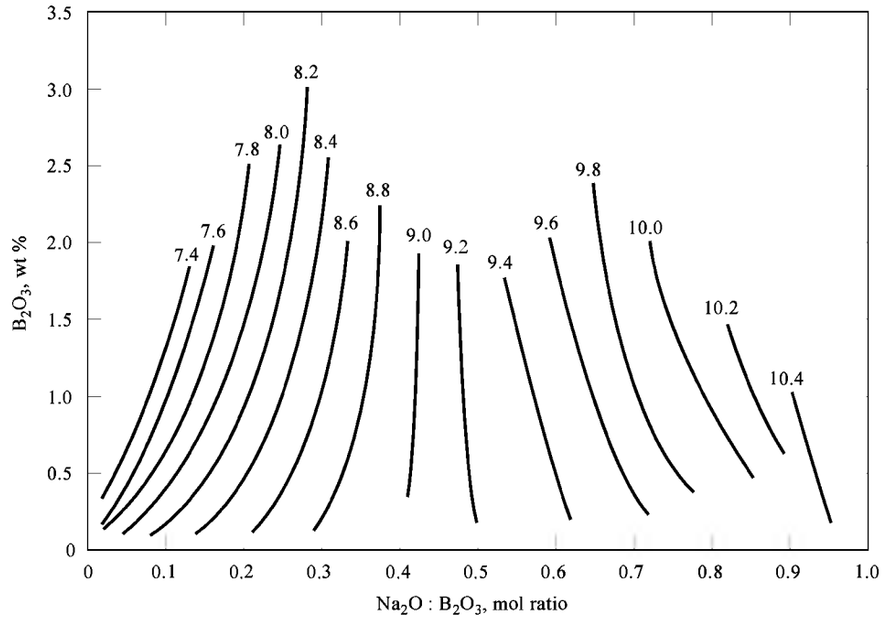


Fig. 2. Values of pH in the system Na_2O–B_2O_3–H_2O at 25°C (61).

This anomalous pH behavior results from the presence of polyborates, which dissociate into $B(OH)_3$ and $B(OH)_4^-$ as the solutions are diluted. Below pH of about 9 the solution pH increases on dilution; the inverse is true above pH 9. This is probably because of the combined effects of a shift in the equilibrium concentration of polymeric and monomeric species and their relative acidities. At a $Na_2O:B_2O_3$ mol ratio equal to 0.41 at pH 8.91, or $K_2O:B_2O_3$ mol ratio equal to 0.405 at pH 9 the pH is independent of concentration. This ratio and the pH associated with it have been termed the isohydric point of borate solutions (62).

The presence of metal salts, particularly those containing alkaline-earth cations and or halides, cause some shifts in the polyborate equilibria. This may result from direct interaction with the boron–oxygen species, or from changes in the activity of the solvent water (63).

Solubility Trends. Formation of polyborates greatly enhances the mutual solubilities of boric acid and alkali borates. Solubility isotherms in the system $Na_2O–B_2O_3–H_2O$ are shown in Figure 3. When borax, $Na_2B_4O_7 \cdot 10H_2O$, is added to a saturated boric acid solution or when boric acid is added to a saturated borax solution, the B_2O_3 weight percent in the solution greatly increases. Polymerization decreases the concentrations of $B(OH)_3$ and $B(OH)_4^-$ in equilibrium with the solid phases, thus permitting more borax or boric acid to dissolve.

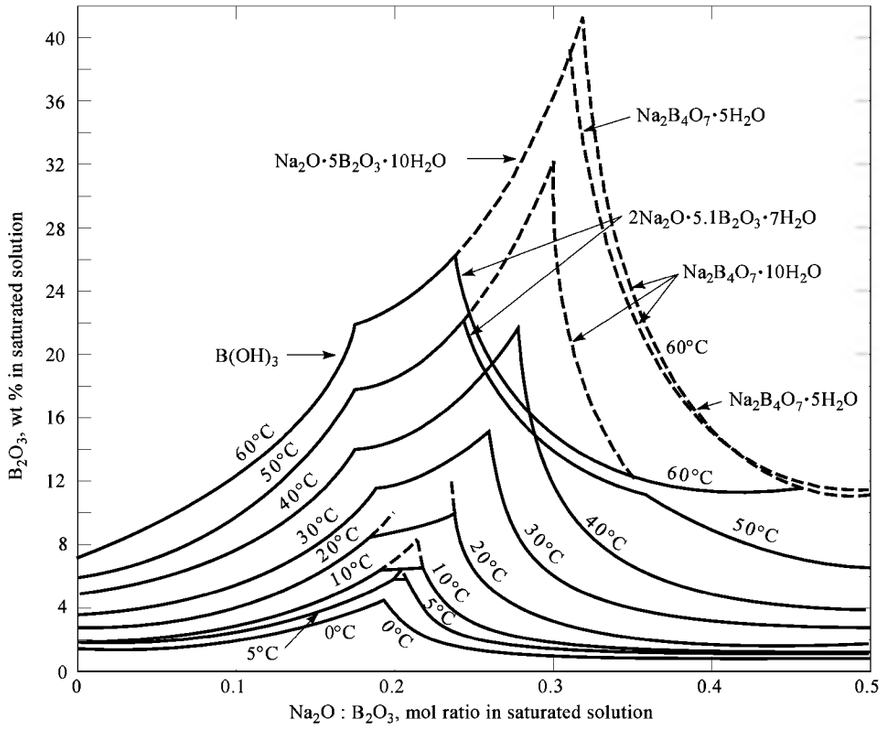


Fig. 3. Solubility isotherms for the system $Na_2B_4O_7–B_2O_3–H_2O$ at 0–60°C. The compound $2Na_2O \cdot 5.1B_2O_3 \cdot 7H_2O$ (Suhr's borate) usually does not appear because it crystallizes very slowly in the absence of seed.

Sodium borate solutions near the $Na_2O:B_2O_3$ ratio of maximum solubility can be spray-dried to form an amorphous product with the approximate composition $Na_2O \cdot 4B_2O_3 \cdot 4H_2O$ commonly referred to as sodium octaborate (64). This material dissolves rapidly in water without any decrease in temperature to form supersaturated solutions. Such solutions have found application in treating cellulosic materials to impart fire-retardant and decay-resistant properties (see CELLULOSE).

The Polyborate Species. From a series of very rigorous pH studies, a series of equilibrium constants involving the species $B(OH)_3$, $B(OH)_4^-$, and the plyions $B_3O_3(OH)_5^{2-}$ *[12344-78-4]*, $B_3O_3(OH)_4^-$ *[12344-77-3]*, $B_5O(OH)_4^-$ *[12343-58-7]*, and $B_4O_5(OH)_4^{2-}$ *[12344-83-1]* have been calculated (65). The relative populations of these species as functions of pH are shown in Figure 4. It is clear that species containing three, four, and five borons are significant at intermediate pH values. The ratio between the total anionic charge and the number of borons per ion increases with increasing pH.

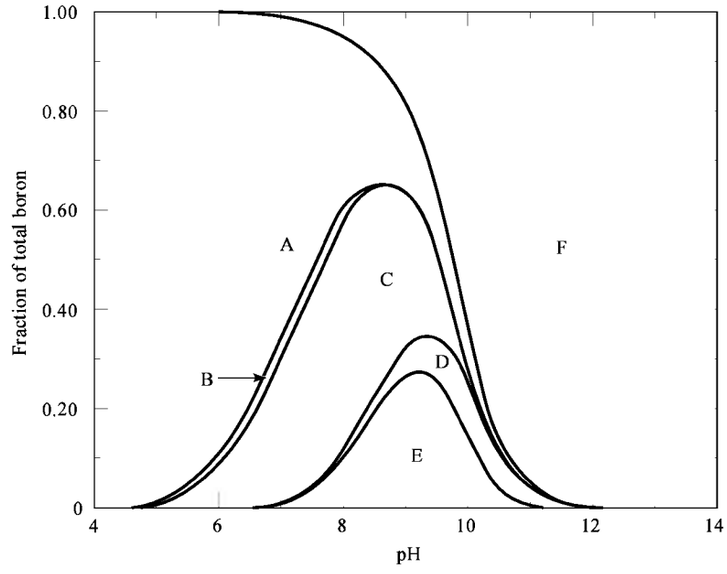
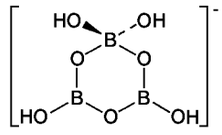


Fig. 4. Distribution of boron in A, $B(OH)_3$; B, $B_5O_6(OH)_4$; C, $B_3O_3(OH)_4$; D, $B_3O_3(OH)_5^2$; E, $B_4O_5(OH)_4^2$; F, $B(OH)_4$; where total B_2O_3 concentration is 13.93 g L. At a given pH, the fraction of the total boron in a given ion is represented by the portion of a vertical line falling within the corresponding range (65).

The polyions postulated in solution all have known structural analogues in crystalline borate salts. Investigations of the Raman (66) and ^{11}B nmr (67) spectra of borate solutions have confirmed the presence of three of these species: the triborate (3), $B_3O_3(OH)$;$_4$, tetraborate (4), $[B_4O_5(OH)^2$;$_4]$, and pentaborate (5) B_5O (OH) ;$_4$, polyanions. Skeletal structures were assigned based on coincidences between the solution spectra and those solid borates for which definitive structural data are available (52). These same ions have been postulated to be present in alkali metal borate glasses as well.



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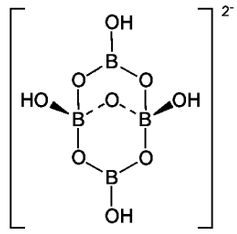

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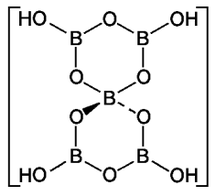


(5)

A rapid equilibrium exists among the various polyborate species in aqueous solutions.

Sodium Borates

Disodium Tetraborate Decahydrate (Borax Decahydrate). Disodium tetraborate decahydrate, $Na_2B_4O_7 \cdot 10H_2O$ or $Na_2O \cdot 2B_2O_3 \cdot 10H_2O$, formula wt, 381.36; monoclinic; sp gr, 1.71; specific heat 1.611 kJ (kg·K) [0.385 kcal (g°C] at 25–50°C (68); heat of formation, 6.2643 MJ mol (1497.2 kcal mol) (69); exists in nature as the mineral borax. Its crystal habit, nucleation, and growth rate are sensitive to inorganic and surface active organic modifiers (70).

The solubility–temperature curves for the Na_2O–B_2O_3–H_2O system are given in Figure 5 (Table 9). The solubility curves of the penta- and decahydrates intersect at 60.6–60.8°C, indicating that the decahydrate, when added to a saturated solution above this temperature, dissolves with crystallization of the pentahydrate and the reverse occurs below this temperature. This transition temperature may be lowered in solutions of inorganic salts, eg, 49.3°C in solutions saturated with sodium sulfate and 39.6°C with sodium chloride. Heats of solution for borax have been determined (67,73) and the manufacturer quotes a value of about 283 kJ kg (67.6 kcal mol) (33).

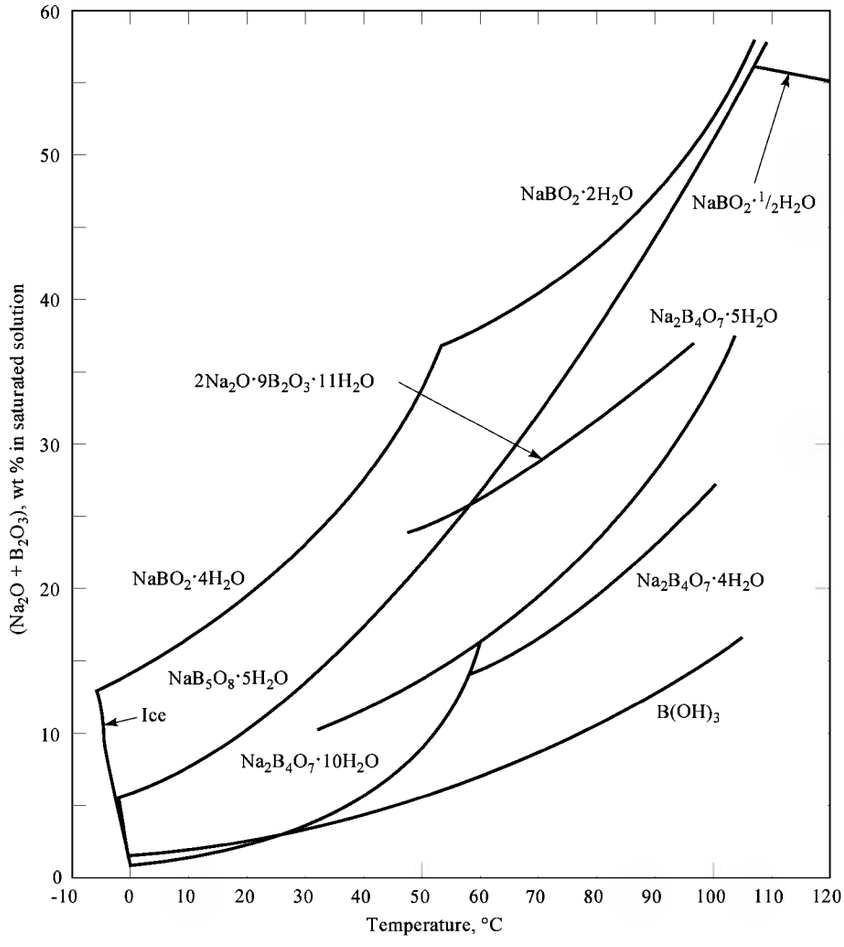


Fig. 5. Solubility–temperature curves for boric acid, borax, sodium pentaborate, and sodium metaborate (71).

Courtesy of The American Chemical Society.

Table 9. Aqueous Solubilities of Alkali Metal and Ammonium Borates at Various Temperatures

Compound	CAS Registry Number	Solubility, wt % anhydrous salt, at °C											
		0	10	20	25	30	40	50	60	70	80	90	100
$Li_2O \cdot 5B_2O_3 \cdot 10H_2O$[a]	*[37190-10-6]*							20.88	24.34	27.98	31.79	36.2	41.2
$Li_2O \cdot 2B_2O_3 \cdot 4H_2O$	*[39291-91-3]*	2.2–2.5	2.55	2.81	2.90	3.01	3.26	3.50	3.76	4.08	4.35	4.75	5.17
$Li_2O \cdot B_2O_3 \cdot 16H_2O$[b]	*[41851-38-1]*	0.88	1.42	2.51	3.34	4.63	9.40						
$Li_2O \cdot B_2O_3 \cdot 4H_2O$	*[15293-74-0]*						7.40	7.84	8.43	9.43	10.58 9.75	11.8	13.4[c]
$Na_2O \cdot 5B_2O_3 \cdot 10H_2O$	*[12046-75-2]*	5.77	7.90	10.55	12.20	13.72	17.50	21.72	26.88	32.25	38.1	44.3	51.0
$Na_2O \cdot 2B_2O_3 \cdot 10H_2O$	*[1303-96-4]*	1.18	1.76	2.58	3.13	3.85	6.00	9.55	15.90				
$Na_2O \cdot 2B_2O_3 \cdot 4.67H_2O$[d]	*[12045-88-4]*								16.40	19.49	23.38	28.37	34.63
$Na_2O \cdot 2B_2O_3 \cdot 4H_2O$[e]	*[12045-87-3]*								14.82	17.12	19.88	23.31	28.22
$Na_2O \cdot B_2O_3 \cdot 8H_2O$[f]	*[10555-76-7]*	14.5	17.0	20.0	21.7	23.6	27.9	34.1					
$Na_2O \cdot B_2O_3 \cdot 4H_2O$	*[16800-11-6]*								38.3	40.7	43.7	47.4	52.4
$K_2O \cdot 5B_2O_3 \cdot 8H_2O$	*[12229-13-9]*	1.56	2.11	2.82	3.28	3.80	5.12	6.88	9.05	11.7	14.7	18.3	22.3
$K_2O \cdot 2B_2O_3 \cdot 4H_2O$	*[12045-78-2]*		9.02	12.1	13.6	15.6	19.4	24.0	28.4	33.3	38.2	43.2	48.4
$K_2O \cdot B_2O_3 \cdot 2.5H_2O$	*[27516-44-5]*		42.3	43.0	43.3	44.0	45.0	46.1	47.2	48.2	49.3	50.3	
$Rb_2O \cdot 5B_2O_3 \cdot 8H_2O$	*[37190-12-8]*	1.58	2.0	2.67	3.10	3.58	4.82	6.52	8.69	11.4	14.3	18.1	23.75[g]
$Cs_2O \cdot 5B_2O_3 \cdot 8H_2O$[h]	*[12229-10-6]*	1.6	1.85	2.5	2.97	3.52	4.8	6.4	8.31	10.5	13.8	18.0	23.45[i]
$(NH_4)_2O \cdot 2B_2O_3 \cdot 4H_2O$	*[10135-84-9]*	3.75	5.26	7.63	9.00	10.8	15.8	21.2	27.2	34.4	43.1	52.7	
$(NH_4)_2O \cdot 5B_2O_3 \cdot 8H_2O$	*[12229-12-8]*	4.00	5.38	7.07	8.03	9.10	11.4	14.4	18.2	22.4	26.4	30.3	

[a] Incongruent solubility below 37.5 or 40.5°C.

[b] Transition point to tetrahydrate, 36.9 or 40°C.

[c] At 101.2°C.

[d] Commonly known as the five hydrate (72), transition point to decahydrate, 60.7°C, 16.6% $Na_2B_4O_7$.

[e] Transition point to decahydrate, 58.2°C, 14.55% $Na_2B_4O_7$.

[f] Transition point to tetrahydrate, 53.6°C, 36.9% $Na_2B_2O_4$.

[g] At 102°C.

[h] Dicesium tetraborate pentahydrate *[12228-83-0]*, $Cs_2O \cdot 2B_2O_3 \cdot 5H_2O$, and dicesium diborate heptahydrate *[66634-85-3]*, $Cs_2O \cdot B_2O_3 \cdot 7H_2O$, also exist. The former has incongruent solubility; the latter has a solubility of 36.8 wt % anhydrous salt at 18°C.

[i] At 101.65°C.

The pH of a borax solution increases slightly with increasing concentration (Table 10) and drops slightly with increasing temperature. The vapor pressures of aqueous saturated borax solutions at various temperatures are (73,74):

Temperature, °C	Pressure, kPa
57.94	17.25
57.99	17.33
58.23	17.51
58.56	17.74
58.82	17.94
58.91	18.05
59.42	18.42

To convert from kPa to mm Hg, multiply by 7.5. Values for the specific heat of aqueous borax solutions as a function of weight percent decahydrate are (73):

Borax decahydrate, wt %	Specific heat, kJ/(kg·K)
1.9	4.13
4.7	4.08
7.2	4.04
9.5	3.99
19.0	3.84
22.8	3.78
26.6	3.71
30.4	3.65
38.0	3.52
45.6	3.57
55.1	3.68

To convert from kJ/(kg·K) to cal/(g·°C), divide by 4.184. The solubilities of borax in organic solvents are given in Table 7.

Table 10. pH of Aqueous Borate Solutions

	Concentration, wt %						
Compound	0.1	0.5	1.0	2.0	4.0	10.0	15.0
$Na_2B_4O_7 \cdot 10H_2O$	9.2	9.2	9.2	9.2	9.3[a]		
$Na_2B_8O_{13} \cdot 4H_2O$			8.5	8.5	8.1	7.6	7.3
$NaB_5O_8 \cdot 5H_2O$			8.5	8.4	8.1	7.6	7.3
$NaBO_2 \cdot 4H_2O$	10.5	10.8	11.0	11.2	11.4	11.8	11.9
$NaBO_2 \cdot 2H_2O$	10.6	10.9	11.1	11.3	11.5	11.8	12.0
$K_2B_4O_7 \cdot 4H_2O$	9.2	9.1	9.1	9.2	9.3		
$KB_5O_8 \cdot 4H_2O$		8.4	8.4	8.3	7.9	7.6	
$NH_4B_5O_8 \cdot 4H_2O$	8.5	8.4	8.3	8.2	7.8	7.3	

[a] Saturated solution, 4.71 wt %.

If borax has been previously warmed to 50°C, it dehydrates reversibly into the pentahydrate and water vapor. The equilibrium vapor pressure for this transition at various temperatures is (74,75): 15°C, 0.933 kPa (7.0 mm Hg); 19.8°C, 1.33 kPa (10.0 mm Hg); 25°C, 1.87 kPa (14.0 mm Hg); 59°C, 17.7 kPa (133.0 mm Hg). If the decahydrate has not been warmed above 50°C, it develops a vapor pressure of only 0.213 kPa (1.6 mm Hg) at 20°C. In this case, when placed over P_2O_5, it does not form the crystalline pentahydrate but decomposes gradually to form an amorphous product having about 2.4 molecules water content.

Heats of dehydration per mole of water vapor are (74) decahydrate to pentahydrate, 54.149 kJ (12.942 kcal), and decahydrate to tetrahydrate, 54,074 kJ (12.924 kcal). Borax stored over a saturated sucrose-sodium sucrose–sodium chloride solution maintains exactly 10 moles of water and can thus be used as an analytical standard. Commercial borax tends to lose water of crystallization if stored at high temperature or in dry air.

A single-crystal x-ray diffraction study has shown that the borate ion present in borax has the formula $[B_4O_5(OH)_4]^{2-}$; (4), the sodium ions occupying two unique sites, and eight moles of water of crystallization and two moles of water existing as hydroxyl groups. The formula is best represented as $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$ (76). The same borate ion (4) exists in the pentahydrate, explaining the ready interconversion of the penta- and decahydrates (77). Slow dehydration of borax results in the loss of eight moles of water between 50 and 150°C.

Rapid heating of either borax decahydrate or pentahydrate causes the crystal to dissolve before significant dehydration, and at about 140°C, puffing occurs from rapid vaporization of water to form particles having as high as 90% void volume and very low bulk density (78).

Disodium Tetraborate Pentahydrate (Borax Pentahydrate). Although referred to as borax pentahydrate, well-formed crystals actually contain not five but 4.67 moles of water, $Na_2B_4O_7 \cdot 4.67H_2O$ or $Na_2O \cdot 2B_2O_3 \cdot 4.67H_2O$. This structure has been confirmed by an x-ray single crystal analysis that showed that two of the three water of crystallization sites are only partially filled (71). The structural formula is best represented as $Na_2[B_4O_5(OH)_4] \cdot 2.67H_2O$; formula wt, 286.78; trigonal; rhombohedral crystal shape; sp gr, measured 1.880, crystallographic 1.912; specific heat, 1.32 kJ/(kg·K) [0.316 kcal/(g·°C)] (68); heat of formation, −4.7844 MJ/mol (−1143.5 kcal/mol) (69). It is found in nature as a fine-grained mineral, tincalconite, formed by dehydration of borax.

Solubility data in water are given in Figure 5 and in Table 9, solution pH in Table 10, and the solubility in organic solvents is given in Table 7. Heats of solution in water have been determined (68,73). The pentahydrate, in contact with its aqueous solution, is metastable with respect to the tetrahydrate (kernite) at temperatures above 58.2°C and metastable to borax decahydrate below 60.6–60.8°C. Kernite can be slowly crystallized from a near saturate

solution heated near the boiling point for several days.

Pentahydrate is reversibly converted to an amorphous dihydrate, at 88°C and 0.26 kPa (2 mm Hg) or by boiling with xylene (73,75). The heat of dehydration for the pentahydrate to tetrahydrate has been calculated to be 53.697 kJ (12.834 kcal) per mole of water (74). Thermogravimetric analyses show that 2.75 moles of water are lost on heating to 140°C. Like borax, pentahydrate puffs when heated rapidly to give a product having a bulk density of 0.042 g mL (79).

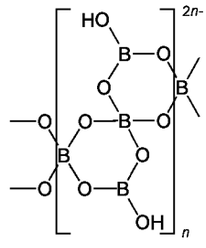
A single-crystal x-ray structure determination has shown that the borate ion in the pentahydrate and in borax are identical (77).

Disodium Tetraborate Tetrahydrate. Disodium tetraborate tetrahydrate, $Na_2B_4O_7 \cdot 4H_2O$ or $Na_2O \cdot 2B_2O_3 \cdot 4H_2O$, formula wt, 273.27; monoclinic; sp gr, 1.908; specific heat, ca 1.2 kJ (kg·K) [0.287 kcal (g·°C)] (61); heat of formation, 4.4890 MJ mol (1072.9 kcal mol) (69); exists in nature as the mineral kernite and has a structural formula $Na_2[B_4O(OH)_2] \cdot 3H_2O$. The crystals have two perfect cleavages and when ground, form elongated splinters.

The water solubility of kernite is shown in Figure 5 and in Table 9. Kernite is the stable phase in contact with its solutions from 58.2°C to ca 95°C (71). Its rate of crystallization is, however, much slower than that of the pentahydrate. Large kernite crystals can be grown slowly by seeding saturated borax solutions.

At relative humidities above 70% kernite absorbs water irreversibly to form borax. Kernite loses water slowly over P_2O_5 in vacuum or by heating at 100–120°C, forming a crystalline dihydrate, metakernite, which reverts to kernite at 60% relative humidity (74).

The structure of kernite consists of parallel infinite chains of the $[B_4O(OH)_2]^{2n-}{}_n$ ion (6) composed of six membered rings (80). The polymeric nature of the anion is consistent with the slow rate of dissolution and crystallization observed for kernite.



(6)

Disodium Tetraborate (Anhydrous Borax). Disodium tetraborate, $Na_2B_4O_7$ or $Na_2O \cdot 2B_2O_3$, formula wt, 201.21; sp gr (glass), 2.367, (α-crystalline form), 2.27; heat of formation (glass), 3.2566 MJ mol (778.34 kcal mol), (α-crystalline form), 3.2767 MJ mol (783.2 kcal mol) (17); exists in several crystalline forms as well as a glassy form (73). The most common α-crystalline form that melts congruently at 742.5°C is obtained by dehydrating borax hydrates and is the stable form above 600–700°C (73). A large amount of heat capacity data has been reported (17,81). Anhydrous borax glass dissolves in water more slowly than the hydrated forms. Heats of solution have been measured (68), and the manufacturer lists a value of 213.8 kJ kg (51.1 kcal kg) (33). The solubilities of finely divided crystalline disodium tetraborate at 25°C expressed as weight percent $Na_2O \cdot 2B_2O_3$ is 16.7% in methanol, 30% in ethylene glycol, and 40.6 g L in formamide (61).

Crystalline anhydrous borax takes up some water from moist air even at 300°C. It becomes anhydrous near 700°C and melts at 742.5°C. The heat of hydration to borax has been calculated as 161 kJ mol (38.5 kcal mol) of $Na_2O \cdot 2B_2O_3$ (73,82). The heat of fusion has been reported as 81.2 kJ mol (19.4 kcal mol) (17).

A single-crystal x-ray diffraction study has shown that the borate anion in anhydrous borax is polymeric in nature and is formed via oxygen bridging of triborate and pentaborate groups (83). The chemistry of anhydrous borax has been reviewed (73,84).

Disodium Octaborate Tetrahydrate. The composition of a commercially available sodium borate hydrate, 66.3 wt % B_2O_3, POLYBOR (64), corresponds quite closely to that of a hypothetical compound, disodium octaborate tetrahydrate, $Na_2B_8O_{13} \cdot 4H_2O$ or $Na_2O \cdot 4B_2O_3 \cdot 4H_2O$. This product dissolves rapidly in water without the temperature decrease, which occurs when the crystalline borates dissolve, and easily forms viscous supersaturated solutions at elevated temperatures. The solution pH decreases as the concentration increases (Table 10). The solubility of the product is shown compared with that of borax (33):

		Concentration, B_2O_3 in saturated solutions, wt %	
Temperature, °C	Solubility, POLYBOR, wt %	POLYBOR	Borax
0	2.4	1.6	0.7
10	4.5	3.0	1.1
20	9.5	6.3	1.7
30	21.9	14.5	2.6
40	27.8	18.4	4.1
50	32.0	21.2	6.5
60	35.0	23.2	11.1
75	39.3	26.0	14.7
94	45.3	30.0	21.0

Sodium Pentaborate Pentahydrate. Sodium pentaborate pentahydrate, $NaB_4O_8 \cdot 5H_2O$ or $Na_2O \cdot 5B_2O_3 \cdot 10H_2O$; formula wt, 295.11; monoclinic; sp gr, 1.713; exists in nature as the mineral sborgite *[12272-01-4]*. Heat capacity, entropy, and other thermal measurements have been made at 15–345 K (85).

Sodium pentaborate can easily be crystallized from a solution having a $Na_2O:B_2O_3$ mol ratio of 0.2. Its water solubility (Fig. 5 and Table 9) exceeds that of borax and boric acid. Its pH decreases with solution concentration (Table 10). It is stable in contact with its own solution between 2 and 59.5°C. When a saturated pentaborate solution is agitated for some time at temperatures near boiling, the compound $2Na_2O \cdot 9B_2O_3 \cdot 11H_2O$, also known as Taylors borate, sp gr, 1.903; crystallizes very slowly if seed is present. Pentaborate pentahydrate, which is metastable to Taylors borate at higher temperatures, readily forms supersaturated solutions and crystallizes as the kinetic product. In the absence of seed crystals, however, the stable phase above 106°C shifts to pentaborates of lower hydration (73).

Crystalline sodium pentaborate pentahydrate is stable in the atmosphere. When heated in vacuum, it is stable to 75°C; however, above 75°C, four of its five H_2O molecules are lost (73).

A single-crystal x-ray diffraction study gives a structural formula of $Na_2[B_5O_6(OH)_4] \cdot 3H_2O$ and contains the pentaborate ion analogous to that found in the corresponding potassium compound (86).

Sodium Metaborate Tetrahydrate. Sodium metaborate tetrahydrate, $NaBO_2 \cdot 4H_2O$ or $Na_2O \cdot B_2O_3 \cdot 8H_2O$; formula wt, 137.86; triclinic; sp gr, 1.743; is easily formed by cooling a solution containing borax and an amount of sodium hydroxide just in excess of the theoretical value. It is the stable

phase in contact with its saturated solution between 11.5 and 53.6°C. At temperatures above 53.6°C, the dihydrate, $NaBO_2 \cdot 2H_2O$, becomes the stable phase. The water solubility of sodium metaborate is given in Figure 5 and in Table 9 and the pH with concentration is given in Table 10.

Heat capacity data for metaborate solutions have been reported (87). The solubility of sodium metaborate tetrahydrate in methanol at 40°C is 26.4 wt % (61).

The relative humidity over a saturated solution of the tetrahydrate at 14–24°C is 90 ± 1%, and the humidity over mixtures of the tetra- and dihydrates is 42% at 22°C; 43% at 24.8°C; 45% at 27.0; and 39% at 91.3°C (88). The heat of hydration for the dihydrate to tetrahydrate conversion has been calculated as 52.51 kJ (12.55 kcal) per mole of water (88). The thermogravimetric curve shows a loss of 0.5 moles of water at 130°C; two moles at 140°C; three moles at 280°C; and the last at temperatures up to 800°C (89).

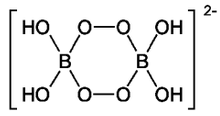
Sodium metaborate absorbs CO_2 from the atmosphere, forming borax and sodium carbonate. Crystals of the tetrahydrate melt in its water of crystallization at about 54°C. The solid-state structure of the tetrahydrate, $Na[B(OH)_4] \cdot 2H_2O$, consists of discrete tetrahedral $B(OH)_4^-$ groups (90).

Sodium Metaborate Dihydrate. Sodium metaborate dihydrate, $NaBO_2 \cdot 2H_2O$ or $Na_2O \cdot B_2O_3 \cdot 4H_2O$; formula wt, 101.83; triclinic; sp gr, 1.909; can be prepared by heating a slurry of the tetrahydrate above 54°C, by crystallizing metaborate solutions at 54–80°C, or by dehydrating the tetrahydrate in vacuum. Large crystals can be grown by heating the solid in its mother liquor for several days. The dihydrate is the stable phase in contact with its saturated solution between 53.6 and 105°C. At higher temperatures a hemihydrate, $NaBO_2 \cdot 0.5H_2O$, is formed (73).

The water solubility for the dihydrate is shown in Figure 5 and in Table 9 and solution pH with concentration is given in Table 10. The solubility of the dihydrate in ethanol is 0.3 wt % at boiling, and in methanol it is 17.8% at 22°C, 19.5% at 40°C, and 24.6% at 60°C (61).

The dihydrate loses water slowly at room temperature. Its heat of dehydration to $NaBO_2 \cdot 0.5H_2O$ has been calculated as 58.1 kJ/mol (13.9 kcal/mol) of H_2O (88). Sodium metaborate dihydrate reacts with atmospheric CO_2 to produce sodium carbonate and borax. The melting point is 90–95°C, compared to 54°C for the tetrahydrate. Some crystallographic work has been done (91).

Sodium Perborate Hydrates. Peroxyborates are commonly known as perborates, written as if the perborate anion were BO_3^-. X-ray crystal structure has shown that they contain the dimeric anion $[(HO)_2B(O_2)_2B(OH)_2]^{2-}$ (7) (92). Three sodium perborate hydrates, $NaBO_3 \cdot xH_2O$ (x = 1, 3, and 4), are known. Only the mono- and tetrahydrate are of commercial importance, primarily as bleaching agents (qv) in laundry products.



(7)

Sodium perborate tetrahydrate, $NaBO_3 \cdot 4H_2O$ or $Na_2B_2(O_2)_2(OH)_4 \cdot 6H_2O$, is triclinic; heat of formation, −2112 kJ/mol (−504.8 kcal/mol) (crystal), −921 kJ/mol (−220.2 kcal/mol) (1 *M* soln); and contains 10.4 wt % active oxygen. It melts at 63°C by dissolving in its own water of hydration and on heating to 250°C decomposes rapidly and completely to oxygen and sodium metaborate. In water its decomposition, which is important in its use as a bleach, is accelerated by catalysts or elevated temperature. Typical solutions at room temperature are unstable and lose active oxygen unless a stabilizer is present. The rate of decomposition increases with pH. The solubility in water is 2.5 wt % $NaBO_3 \cdot 4H_2O$ at 20°C and 3.6 wt % at 29°C (93). The solubility is enhanced by certain polyhydroxy compounds which form complexes with borates, such as tartaric acid, citric acid, mannitol, glycerol, and most significantly, by alkali polyphosphates. Dilute solutions contain the monoperoxyborate anion, $B(OH)_3(OOH)^-$. More concentrated solutions contain this anion plus $B(OH)_2(OOH)_2^-$, $B(OH)(OOH)_3^-$, $B(OOH)_4^-$, and polyperoxyborate anions (94).

Commercial preparation of sodium perborate tetrahydrate is by reaction of a sodium metaborate solution, from sodium hydroxide and borax pentahydrate, and hydrogen peroxide followed by crystallization of tetrahydrate (95). The trihydrate and monohydrate can be formed by reversible dehydration of the tetrahydrate.

Sodium perborate trihydrate, $NaBO_3 \cdot 3H_2O$ or $Na_2B_2(O_2)_2(OH)_4 \cdot 4H_2O$, triclinic, contains 11.8 wt % active oxygen (96). It has been claimed to have better thermal stability than the tetrahydrate but has not been used commercially. The trihydrate can be made by dehydration of the tetrahydrate or by crystallization from a sodium metaborate and hydrogen peroxide solution in the present of trihydrate seeds. Between 18 and 50°C the trihydrate is more stable but slower to crystallize than the tetrahydrate. Below 15°C the trihydrate is spontaneously converted into the tetrahydrate.

Sodium perborate monohydrate, $NaBO_3 \cdot H_2O$ or $Na_2B_2(O_2)_2(OH)_4$, 16.0 wt % active oxygen, is commercially prepared by dehydration of the tetrahydrate. The monohydrate has the same peroxyborate anion (7), as the higher hydrates and is the anhydrous sodium salt of this anion. Further dehydration results in decomposition of the peroxyborate.

Analysis. The alkali metal and ammonium borates are analyzed for M_2O and B_2O_3 content by dissolving the compound in water, titrating the M_2O content with dilute HCl and determining the B_2O_3 content by complexation with excess mannitol followed by titration with dilute NaOH (97). The B_2O_3 content for calcium borates and other borates of low water solubility is determined by extraction into acid solution followed by mannitol complexation and titration with dilute base. The commercial hydrates are often overdried, leading to apparent B_2O_3 assays over 100%.

Borate reacts with curcumin *[458-37-7]*, $C_{21}H_{20}O_6$, in the presence of a mineral acid to give a colored 1:2 borc acid: curcumin complex that has been used to determine microamounts of boron. Carminic acid *[1260-17-9]*, $C_{22}H_{20}O_{13}$, (98) and azomethine-H (99) also form a colored complex useful for low level detection of borates. Boron compounds give a characteristic green color when burned in a flame.

Methods for analysis of industrial borate chemicals have been reviewed (100).

Manufacture.

Borax Decahydrate and Pentahydrate. Borax decahydrate and pentahydrate are produced from sodium borate ores, dry lake brines, colemanite, or magnesium borate ores.

Production from sodium borate ores takes place in the United States, Turkey, and Argentina. All U.S. production based on sodium borate ores is from the United States Borax & Chemical Corp. in Boron, California. Turkish mining of tincal takes place at Kirka. This operation is under the control of the Turkish government and its representative, Etibank. Argentine production is carried out at Tincalayu, primarily by Boroquimica Samicaf.

At the production facility in Boron, California, United States Borax & Chemical Corp. operates an open-pit borax mine and a refinery. This facility represents the largest single source of borate chemicals in the world. In the mine, overburden is blasted and hauled to storage areas in 154-metric ton electric trucks. Tincal and kernite ores are mined separately. The ore is drilled, blasted, and trucked to an impact mill where it is crushed to <20.3 cm. Kernite, which dissolves slowly in process liquors, is crushed, wet with water, stacked, and allowed to hydrate to more rapidly soluble borax. Crushed tincal ore and the hydrated kernite consisting primarily of borate mineral and clay are conveyed on a belt and blended to constant B_2O_3 content on a surface stockpile. It is then crushed to <1.0 cm and sent by belt to a dissolving plant where it is mixed with hot recycle liquor. Liquor leaving the dissolvers is passed over vibrating screens that remove rocks and clay particles larger than 0.25 mm (60 mesh). The liquor and fine insolubles are then fed to a primary thickener for settling. There are four thickener stages operating in a countercurrent fashion so that the underflow from each thickener is washed by a progressively weaker borax liquor. Water is added to the fourth thickener to wash the underflow mud, which is then dewatered in a high speed centrifuge. Strong liquor from the primary thickener is pumped to continuous vacuum crystallizers to separate borax pentahydrate. Crystallizer capacity is also maintained for production of borax decahydrate. The crystallizer slurries are dewatered on continuous centrifuges, and the products are dried in rotary and fluid-bed driers. Liquid effluent is pumped into sealed evaporation ponds where borax crystallizes and is recovered. Combined plant capacity for all

products expressed as B_2O_3 is 765,000 metric tons per year.

The source of Argentine production is an open-pit tincal mine at 4000 m above sea level. A modern plant is located near the mine site. Total production of sodium borates is approximately 200,000 metric tons per year (101).

Etibank is the sole producer of boron minerals and derivatives in Turkey, which is second in production only to the United States. The open-pit Kirka mine in the Eskisehir Province is the only source of Turkish sodium borate ore. A tincal concentrate is produced from ore that has been blasted and carried in trucks to the concentration plant. The ore is screened and crushed to reduce it to 100 mm and then hammer milled to 25 mm. The stockpiled material is further milled and screened to 6 mm. A fraction of 1 mm (18 mesh, U.S. Standard) is washed and classified to remove fine clay. Clay is removed from the 1 mm faction by passing it through cyclones and then through a classifier. This material is centrifuged and combined with the washed 1 mm faction to produce a final product which is a 6 mm concentrate having 6–8 wt % moisture and 32% B_2O_3 (102). In 1987 production was reported to be 390,000 metric tons of concentrate (103).

The derivatives plant is designed to annually produce 160,000 t of borax pentahydrate, 17,000 t of borax decahydrate, and 60,000 t of anhydrous borax. A reported 50,000 t of borax pentahydrate was produced in 1987. A sodium borate refinery is fed from stockpiled tincal ore or product from the concentration plant. The feed is dissolved using steam to give a solution 18% in B_2O_3. The solution is then passed through a series of filters and sent to a 1000 ton storage tank. This solution is fed to a vacuum crystallizer where borax pentahydrate is crystallized at 60°C. The wet cake is sent to hydrocyclones followed by centrifuges for dewatering. The borax decahydrate circuit is similar but with a crystallizer operating temperature of 46°C. Moist cake is further dried in rotary driers. Part of the decahydrate is sent to the fusing plant where it is melted at 1100°C to produce anhydrous borax. The cooled glassy material is crushed and screened.

North American Chemical Co. produces borax pentahydrate and decahydrate from Searles Lake brines in both Trona and West End, California (see CHEMICALS FROM BRINES). The 88 km^2 dry lake consists of two brine layers, the analyses of which are given in Table 11. Two distinct procedures are used for the processing of upper and lower lake brines. Borax is produced in Trona from upper lake brines by an evaporative procedure involving the crystallization of potash and several other salts prior to borax crystallization as the pentahydrate (104). A carbonation process is used in West End, California to derive borate values from lower lake brines (105). Raw lower structure brine is carbonated to produce sodium bicarbonate, which is calcined and recrystallized as sodium carbonate monohydrate. The borate-rich filtrate is neutralized with lake brine and refrigerated to crystallize borax.

Table 11. Brine Analyses from Searles Lake

Constituent	Upper structure brine, wt %	Lower structure brine, wt %
KCl	4.90	3.50
Na_2CO_3	4.75	6.50
$NaHCO_3$	0.15	
$Na_2B_4O_7$	1.58	1.55
$Na_2B_2O_4$		0.75
Na_2SO_4	6.75	6.00
Na_2S	0.12	0.30
Na_3AsO_4	0.05	0.05
Na_3PO_4	0.14	0.10
NaCl	16.10	15.50
H_2O[a]	65.46	65.72
WO_3	0.008	0.005
Br	0.085	0.071
I	0.003	0.002
F	0.002	0.001
Li_2O	0.018	0.009

[a] Determined by difference.

Chinese production of borates is from szaibelyite deposits in Liaotung peninsular of Liaoning province of northeast China.

Production of borax from the reaction of colemanite and sodium carbonate is carried out in Spain, Italy, and Poland. Turkish production from colemanite has been discontinued in favor of direct production from tincal ore. Sodium borates are produced in Russia from datolite and in Kazakhstan from szaibelyite.

Anhydrous Borax. Anhydrous borax is produced from its hydrated forms, borax decahydrate or pentahydrate, by fusion (Fig. 6). Low temperature calcining is usually an intermediate step to remove water of hydration. This material is fed to a refractory brick-lined furnace and fused to a mobile liquid at about 1000°C.

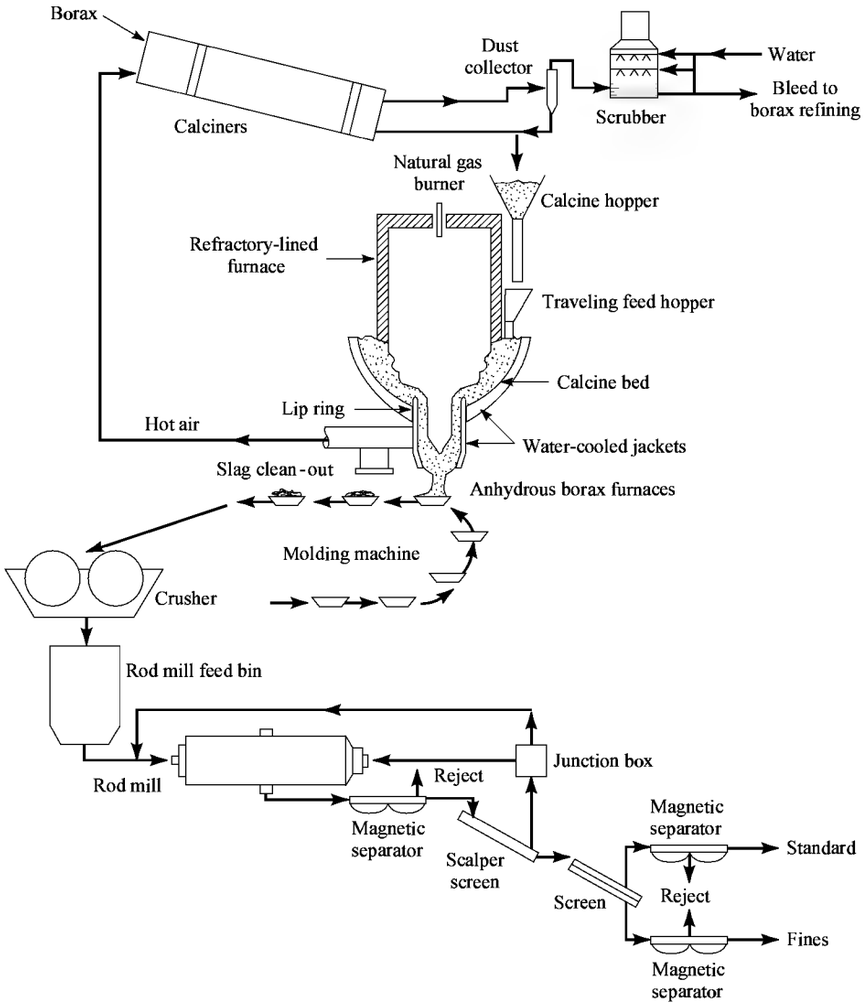


Fig. 6. Flow sheet for the production of anhydrous borax (standard and fines) at Searles Lake, Trona, California (105).

Courtesy of The American Chemical Society.

To produce amorphous anhydrous borax, the molten borax is run between two large water-cooled rolls, forming sheets about 1.6 mm thick, which are then crushed and screened to the desired particle size. Because the borax is cooled rapidly by the rolls, it remains largely amorphous, though it may contain some crystalline anhydrous borax.

In general, the production of fused materials is much more energy intensive than that of hydrated products, and this difference is reflected in their prices. The primary producers are the United States Borax & Chemical Corp. and the North American Chemical Co. Yearly fusion capacities for the two companies are reported to be 86,000 and 36,000 metric tons B_2O_3, respectively (6). There is a plant in Turkey designed for the production of 60,000 t yr of refined anhydrous borax from tincal ore (102). Small quantities of anhydrous borax have been produced in Argentina.

Sodium Perborate. The common commercial practice for the manufacture of sodium perborate tetrahydrate involves the reaction of sodium metaborate and hydrogen peroxide and subsequent crystallization of sodium perborate tetrahydrate. Borax and sodium hydroxide are added to recycled mother liquor to make a strong (150–600 g L) metaborate solution at an elevated (40 to 90°C) temperature. Insoluble impurities are removed by settling and filtration. Metaborate liquor cooled to room temperature is mixed with hydrogen peroxide in an agitated crystallizer and the exothermic heat of reaction is removed by evaporation or refrigerative cooling. The sodium perborate tetrahydrate is separated by filtration or centrifugation. The product crystals are very sensitive to trace impurities such as silica, carbonate, magnesium, calcium, organic compounds, and transition metals that affect properties such as the crystal habit, crystal strength, caking, and stability. Sodium perborate monohydrate is commercially prepared by thermal dehydration of the tetrahydrate or reaction of a sodium metaborate and hydrogen peroxide solution in a fluidized-bed dryer at 45–85°C (106).

Other Sodium Borates. SOLUBOR, TIM-BOR, or POLYBOR (63), proprietary products of United States Borax & Chemical Corp., have the approximate composition of disodium octaborate tetrahydrate, $Na_2O \cdot 4B_2O_3 \cdot 4H_2O$. This material is produced by spray-drying mixtures of borax and boric acid.

Whereas there is no commercial production of sodium pentaborate pentahydrate, the compound can be prepared by crystallizing a borax–boric acid solution having a $Na_2O:B_2O_3$ mol ratio of 0.2.

Sodium metaborate tetrahydrate can be prepared by cooling a solution containing borax and an amount of sodium hydroxide just in excess of the theoretical amount. The dihydrate is prepared by United States Borax & Chemical Corp. by mixing appropriate quantities of borax penta- or decahydrate hydrate and aqueous NaOH to give a 46 to 52% solution concentration of $Na_2O \cdot B_2O_3$ (107). The mixture is then heated to about 90°C to dissolve all solids and slowly cooled to 60–75°C. Crystals of the dihydrate are then harvested and dried.

Product Specifications. Specifications for the maximum allowable impurity levels for borate products are given in Table 12. Where maximum levels are not set, typical values are given. Typical levels of impurities generally fall well below the maximum specification. Both borax decahydrate and pentahydrate are sometimes overdried in manufacture and may give higher than theoretical assays.

Table 12. Maximum Impurity Specifications for Borates[a], wt %

Chemical	Grade[b]	Cl	SO_4^{2-}	Fe_2O_3	Na^+	Ca^{2+}	Heavy metals as Pb	H_2O insolubles
$Na_2O \cdot 2B_2O_3 \cdot 10H_2O$	T	0.07	0.06	0.003				0.02
	SQ[c]	0.4[d]	1.0[d]	2.8[d]		50[d]	10[d]	10[d]

$Na_2O \cdot 2B_2O_3 \cdot 5H_2O$	T	0.05	0.08	0.004				
$NaBO_2 \cdot 4H_2O$	T	0.1	0.1	0.003		0.002[e]	0.0005[e]	0.002[e]
$NaBO_2 \cdot 2H_2O$	T	0.1	0.1	0.007		0.003[e]	0.0005[e]	0.002[e]
$K_2O \cdot 2B_2O_3 \cdot 4H_2O$	T	0.05	0.05	0.0014	0.10	0.002[e]	0.0005[e]	0.002[e]
$KB_5O_8 \cdot 4H_2O$	T	0.05	0.05	0.003	0.10		0.0005[e]	
$(NH_4)_2O \cdot 2B_2O_3 \cdot 4H_2O$	T	0.05	0.05	0.0014	0.0026[e]			
$NH_4B_5O_8 \cdot 4H_2O$	T	0.05	0.05	0.0014			>0.0001[e]	
	SQ	0.4[d]	1[d]	5[d]			2[d]	10[d]

[a] Ref. 33.

[b] T technical and SQ special quality.

[c] Also contains 10 ppm phosphate.

[d] Values are ppm.

[e] Maximum values are not set. These are typical values.

NF-grade borax decahydrate is manufactured to conform to standards of the *National Formulary*, XV ed., for sodium borate. Maximum allowable impurity levels for technical anhydrous borax are SO^2 ;$_4$, 0.41% ; SiO_2, 0.21% ; Al_2O_3, 0.14% ; CaO, 0.03% ; MgO, 0.15% ; and Fe_2O_3, 0.02% .

Many of the borate chemicals are sold in a variety of particle size distributions, and average size analyses for the various cuts are available from the manufacturer.

Economic Aspects. Table 13 summarizes prices and shipping methods for the principal borate products as of January 1991. Within the United States most shipments are by rail, and additional charges are made for split cars, truck shipments, palletized shipments, etc. Prices are fob Southern California. In general, the borates are stable solids and require no special handling techniques with the possible exception of dust collection.

Table 13. 1991 Prices per Metric Ton for Carload (>18 t) Quantities of Borate Chemicals, U.S. Dollars[a]

Chemical	Grade[b]	Form[c]	Bulk	45.4 kg Paper sacks	Large drums (148 kg)
$Na_2O \cdot 2B_2O_3 \cdot 10H_2O$	T	G	264	314	
	T	P		380	
	T	F		446	
	NF	G		1452	1562
	NF	P			1782
	NF	I			2222
	SQ	G		1892	2002
	SQ	P			2222
$Na_2O \cdot 2B_2O_3 \cdot 5H_2O$	T	G	304	353	
	T	P		419	
$Na_2O \cdot 2B_2O_3$	T		787	836	
	T	glass		1757	
$Na_2O \cdot 4B_2O_3 \cdot 4H_2O$[d]	T			1144	
$NaBO_2 \cdot 4H_2O$	T			1078	
	Ph			1166	
$NaBO_2 \cdot 2H_2O$	T			1408	
	Ph			1496	
$K_2O \cdot 2B_2O_3 \cdot 4H_2O$	T	G		3080	3190
	T	P		3300	3410
$K_2O \cdot 5B_2O_3 \cdot 8H_2O$	T	G		2860	2970
	T	P			3300
$(NH_4)_2O \cdot 2B_2O_3 \cdot 4H_2O$	T	G			2508
	T	P			2838
$(NH_4)_2O \cdot 5B_2O_3 \cdot 8H_2O$	T	G		2090	
	T	P			2530
	SQ	G		2376	2486

[a] Ref. 33.

[b] Grades are T – technical, SQ – special quality, NF – *National Formulary*, and Ph photo.

[c] Forms are G – granular, F – fine powdered, I – impalpable, P – powdered.

[d] POLYBOR.

Decahydrate, Pentahydrate, and Anhydrous Borax and Bulk Calcium Borates. The bulk borate products, borax decahydrate and pentahydrate, anhydrous borax, boric acid and oxide, and upgraded colemanite and ulexite, account in both tonnage and monetary terms for over 99% of sales of the boron primary products industry (6). Economic considerations for all these products are highly interrelated, and most production and trade statistics do not distinguish the various products.

The total tonnages of borate chemicals produced by the world's principal producing countries are given in Table 14. The United States and Turkey are the two most important producers. The United States imported about 24,000 metric tons of Turkish colemanite in 1990 (101).

Table 14. Annual World Borate Production,[a] 10^3 t

	Year					
Country	1985	1986	1987	1988	1989	1990[b]
United States	1151	1135	1256	1149	1114	1094
Turkey	954	928	980	1231	1175	1200
Russia[b]	200	200	200	200	200	175
Argentina	158	192	185	270	261	260

China[b]	27	27	27	27	27	27
Chili	5	6	13	32	131	132
Peru	10[b]	23	23	15[b]	18[b]	18

[a] Ref. 101.

[b] Estimated.

In 1986, Turkey produced nearly one million metric tons of mineral concentrate, whereas production of refined borate chemicals was 89,500 metric tons. Annual production capacities of chemicals at Eskiseher were pentahydrate borax, 160,000 t; anhydrous borax, 60,000 t; and decahydrate borax, 17,000 t. Capacities at Bandermes were decahydrate borax, 55,000 t; boric acid, 33,000 t; and sodium perborate, 64,000 t (103).

Production and export data for U.S. borates are given in Table 15. Most United States exports are shipped to Europe, via Rotterdam, the Netherlands. In 1989 exports of borates from the United States were, in decreasing order (101): the Netherlands, Japan, Canada, Spain, Mexico, Taiwan, and South Korea.

Table 15. Annual Production and Exports of U.S. Borates, 10^3 t[a]

Production and exports	1985	1986	1987	1988	1989	1990
total production						
gross[b]	1151	1135	1256	1149	1114	1094
B_2O_3	577	571	625	578	562	608
exports						
boric acid[c]	44	38	61	56	42	39
refined sodium borates	565	566	552	546	646	585

[a] Ref. 101.

[b] Minerals and compounds sold or used by producers.

[c] Includes orthoboric and anhydrous boric acid.

In 1988 the percentages of exports of both mineral and refined chemicals from Turkey were (6) United States, 23%; Italy, 14%; France, 9%; Japan, 8%; United Kingdom, 7%; Spain, 7%; and West Germany, 5%. Of the exported borates, about 87% were mineral concentrates; the remaining 13% was refined borate chemicals. Small quantities of borates have more recently been exported to the West from Russia. Most of Argentina's production is sold in South America. A new source of potassium, lithium, and boron is being developed in northern Chili by Minsal. The deposit is a thick salt brine where harvesting is expected to be by sequential evaporation in solar ponds. The boron, produced as boric acid, is expected to have an eventual capacity of 17,000 t yr B_2O_3 equivalent. Minera del Boro and Quiborax mine ulexite that is either refined as boric acid or sold as a concentrate (108).

U.S. demand for borate products in 1988 and 1989, determined as B_2O_3, was 355,000 and 315,000 t, respectively (98). The predicted demand for 1993 is from 365,000 to 422,000 t (6).

After a period of growth between 1982 and 1988, demand for borate minerals and compounds was slow in 1988–1991, largely because of the general world economic recession resulting in reduced demand for borosilicate glass fibers for insulation and reinforcement fiber glass. Other reasons for the decline include the reduction of sodium perborate used in detergent powders as use of liquid detergents increased, decline in the use of B_2O_3 as a fire retardant in cellulosic insulation, as well as a decline in agricultural usage as the number of farms decreased. Because of recent concern for the effects of chlorine on the environment (see ALKALI AND CHLORINE PRODUCTS), increasing amounts of sodium perborate are now being added to detergents in the United States (6,101).

World consumption of borate minerals in 1988 was: United States, 491,000 t; Western Europe, 395,000 t; Turkey, 63,000 t; and Japan, 21,000 t (6). U.S. consumption of boron minerals (as B_2O_3) was 315,000 t in 1989 and 319,000 t in 1990 (101).

Since 1970, the price per ton for bulk quantities of technical-grade borax pentahydrate from United States producers has changed dramatically. Prices for technical-grade borax pentahydrate fob works were $83 t in 1970, $116 t in 1975, $186 t in 1980, $236 t in 1985, and $254 t in 1990 (101). The cost, however, has remained fairly steady in constant dollars. In 1984, colemanite was priced at about $226 t fob Turkey. In 1989 Turkish colemanite was $484 per metric ton fob Kings Creek, South Carolina from importer American Borate Co. (6).

There are two U.S. producers of sodium perborate. E. I. du Pont de Nemours & Co., Inc., in Memphis, Tennessee has converted part of their tetrahydrate capacity into monohydrate production (109). Interox has a monohydrate plant with a capacity of 20,000 t in Deer Park, Texas (109,110). 1991 U.S. consumption of sodium perborate was about 27,000 t, compared with about 45,000 t in the mid-1970s.

Europe uses much more sodium perborate than the United States, having an annual consumption of 400,000 t. Perborate has traditionally been used in powdered detergents in Europe because of increased effectiveness in higher (>60°C) temperature European detergent washwater, compared with about 38°C in the United States (111). The increase in demand for the monohydrate (over tetrahydrate) in Europe results from the decreased use of phosphate in detergent formulations. Tetrahydrate is less stable in low phosphate detergents and the monohydrate has a more rapid rate of solution. Growth of the perborate market in the United States comes from the introduction of washing detergents containing perborate as a color-safe bleaching agent. Worldwide demand for monohydrate doubled between 1987 and 1989 and is expected to grow rapidly (110). Prices for sodium perborate tetrahydrate ran from $0.86–$0.96 kg fob Los Angeles, California (Degussa) to $0.80–$0.86 kg fob Memphis, Tennessee (Du Pont) in 1991, prices for the monohydrate ranged from $1.45 kg to $1.56 kg fob Los Angeles, California (Degussa).

Other Sodium Borates. Prices for disodium octaborate tetrahydrate (SOLUBOR, TIM-BOR, POLYBOR), sodium metaborate tetrahydrate, and sodium metaborate dihydrate in 1985 were $924 t, $880 t, and $1034 t, respectively. The corresponding prices in 1990 were $1056 t, $990 t (technical grade), and $1298 t (technical grade), respectively (33).

Health and Safety. Cases of industrial intoxication on exposure to inorganic borates have not been reported (112). There is a large body of literature on the toxicology of boric acid and borax (113). Acute oral LD_{50} in the rat is 3000–4000 mg kg for boric acid and 4500–6000 mg kg for borax (58). These values are comparable to sodium chloride, LD_{50} 3750 mg kg. Ingested boric acid is excreted rapidly in the urine with a half-life of 21 h (114). Chronic ingestion studies (high dosage level and repeated exposure) indicates some reproductive toxicity in animals, but adequate evidence for these effects in humans is lacking (115). Studies indicate no evidence of carcinogenic (116) or mutagenic activity (117). Boric acid and borax are poorly absorbed through healthy skin and do not cause skin irritation. A permissible exposure limit (PEL) of 10 mg m^3 of sodium borate dust has been adopted by OSHA in the United States (118).

Sodium metaborate hydrates are more alkaline than borax and greater care is required in handling. The metaborate material is harmful to the eyes and can cause skin irritation. Gloves, goggles, and a simple dust mask should be used when handling sodium metaborate powder.

Boron in the form of borate is an essential micronutrient for the healthy growth of plants and is present in the normal daily human diet at an estimated level of 3–40 mg as boron. It is not a proven essential micronutrient for animals (119).

The handling of boric acid and borax is generally not considered dangerous. There are no fire risks associated with the storage or use of inorganic borates, and they are not explosive.

Uses. The primary uses of the various borate ores and their derivative products are given in Figure 7. In the United States over 54% of the total B_2O_3 consumption is for glass (qv) manufacture. Approximately 24% is used in fiber glass insulation where the borate is added to increase fiber durability. Approximately 16% is used in textile fiber glass where the B_2O_3 is added to aid in weathering resistance. Other glass applications also use B_2O_3, eg, the production of borosilicate glasses, where the B_2O_3 imparts a low coefficient of thermal expansion, ie, Pyrex glass.

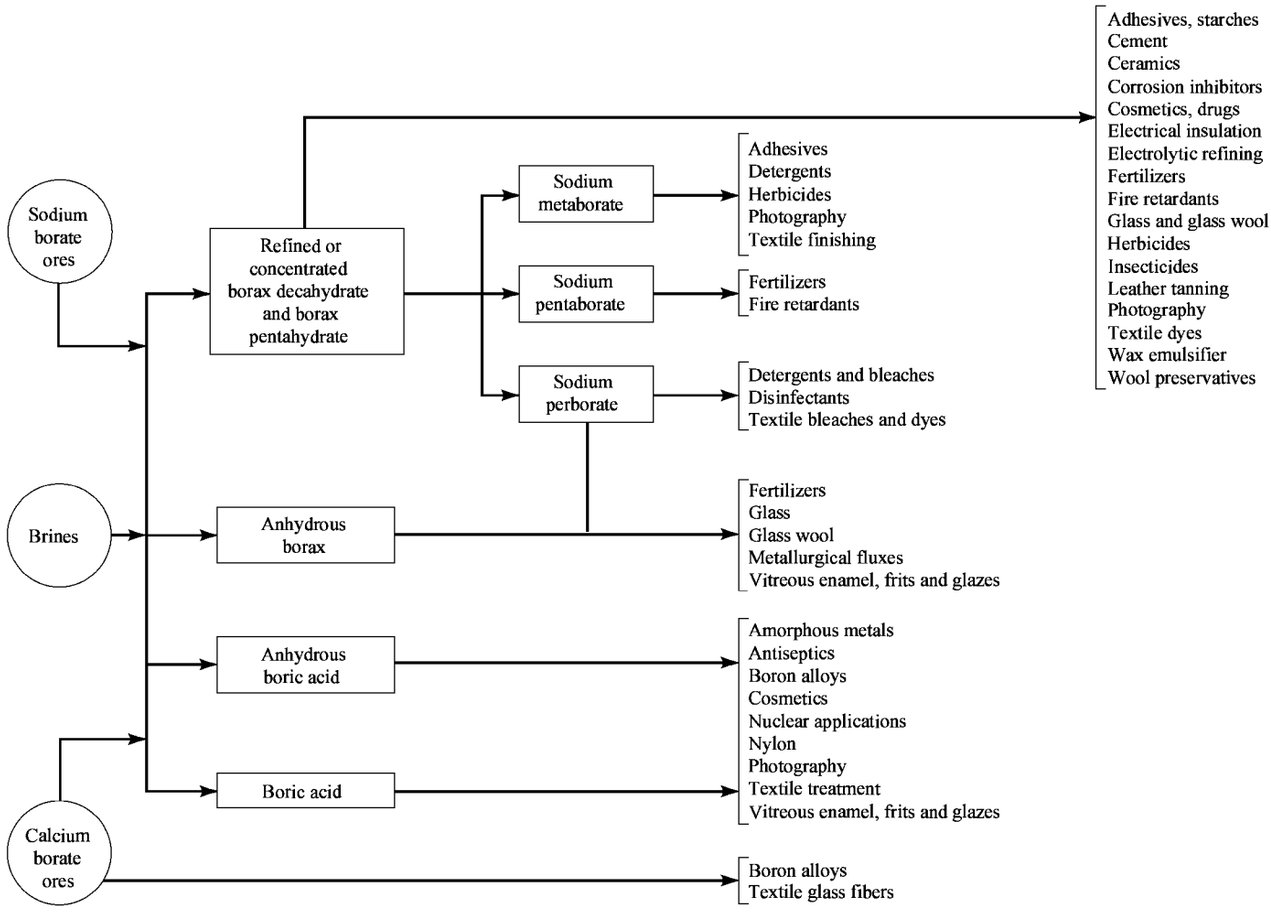


Fig. 7. Uses of boron compounds (57).

Courtesy of British Sulphur Corp.

Borates are used as fluxing agents for porcelain enamels and ceramic glazes (see CERAMICS; ENAMELS, PORCELAIN AND VITREOUS). This market accounts for about 3% of the total usage for the United States. Approximately 8% of total consumption goes into soap and cleaning compositions. Borax is sold both in pure form and as a principal constituent in many household laundry aids and sweeteners. In these applications the germicidal and water-conditioning properties of borax are put to use. Sodium perborate is the active ingredient in a number of dry, nonchlorine bleaches (see SURFACTANTS).

Approximately 5% of the U.S. consumption of B_2O_3 is in agriculture. Boron is a necessary trace nutrient for plants and is added in small quantities to a number of fertilizers. Borates are also used in crop sprays for fast relief of boron deficiency. Borates, when applied at relatively high concentration, act as nonselective herbicides. Small quantities of borates are used in the manufacture of alloys and refractories (qv). Molten borates readily dissolve other metal oxides; usage as a flux in metallurgy is an important application. Other important small volume applications for borates are in fire retardants for both plastics and cellulosic materials, in hydrocarbon fuels for fungus control, and in automotive antifreeze for corrosion control (see CORROSION AND CORROSION INHIBITORS). Borates are used as neutron absorbers in nuclear reactors. Several borates, which are registered with the Environmental Protection Agency (EPA) can be used for insecticidal purposes, eg, TIM-BOR.

The European pattern of borate consumption is different from that of the United States (6). Over 32% of the consumption is as perborate bleach and 47% is used for glass and ceramics.

Disodium Tetraborate Decahydrate. In the United States, nearly all the refined borax is used for household cleaning products. Small amounts are used as fertilizers and herbicides. USP-grade borax is used in cosmetic and toilet goods, in which purity is demanded. Special quality-grade borax is used in electrolytic capacitors, in nuclear applications, and as a laboratory chemical.

Disodium Tetraborate Pentahydrate. Refined pentahydrate consumed in the United States is used in insulation fiber glass, glass, fertilizers, and herbicides. Smaller amounts are used in antifreeze (see ANTIFREEZES AND DEICING FLUIDS), ceramic glazes, and cleaning agents. About 40% of the pentahydrate produced in the United States is exported (101). A large-scale application of this chemical is in the preparation of perborate bleaches.

Disodium Tetraborate. In the United States, anhydrous borax finds most application in the glass industry for enamels, borosilicate glass, and fiber glass insulation. It is also used as an antifreeze additive and as an algicide in industrial water.

Disodium Octaborate Tetrahydrate. Commercially available products, having the approximate composition of a hypothetical disodium octaborate tetrahydrate, have found application in wood (qv) preservatives, fertilizer sprays, insecticides, herbicides, and fire retardants. In many applications the large water solubility of these products is an asset.

Disodium octaborate tetrahydrate (TIM-BOR) is registered for a variety of pests including termites, wood destroying beetles, and carpenter ants. This same compound is also used to control fly larvae in manure piles and is marketed as POLYBOR 3 for this application.

Disodium octaborate tetrahydrate is also used to protect wood from wood destroying fungi and pests. Whereas it has mainly been used for this application in New Zealand, it is being introduced into the United States for this use.

Sodium Metaborate Tetrahydrate and Dihydrate. The sodium metaborates are components in textile finishing, sizing and scouring compositions, adhesives, and detergents. They are also used in many photographic applications. In agriculture they are used in both herbicides and fertilizer sprays. The dihydrate is less affected by heat.

Other Alkali Metal and Ammonium Borates

Dipotassium Tetraborate Tetrahydrate. Dipotassium tetraborate tetrahydrate, $K_2B_4O_7 \cdot 4H_2O$ or $K_2O \cdot 2B_2O_3 \cdot 4H_2O$, formula wt, 305.49; orthorhombic; sp gr, 1.919; is much more soluble than borax in water. Solubility data are given in Table 9; pH with concentration is given in Table 10.

Phase relationships in the system $K_2O–B_2O_3–H_2O$ have been described and a portion of the phase diagram is given in Figure 8. The tetrahydrate, which can be dried at 65°C without loss of water of crystallization, begins to dehydrate between 85 and 111°C, depending on the partial pressure of water vapor in the atmosphere. This conversion is reversible and has a heat of dehydration of 86.6 kJ mol (20.7 kcal mol) of H_2O. Thermogravimetric curves indicate that two moles of water are lost between 112 and 140°C, one more between 200 and 230°C and the last between 250 and 290°C (121).

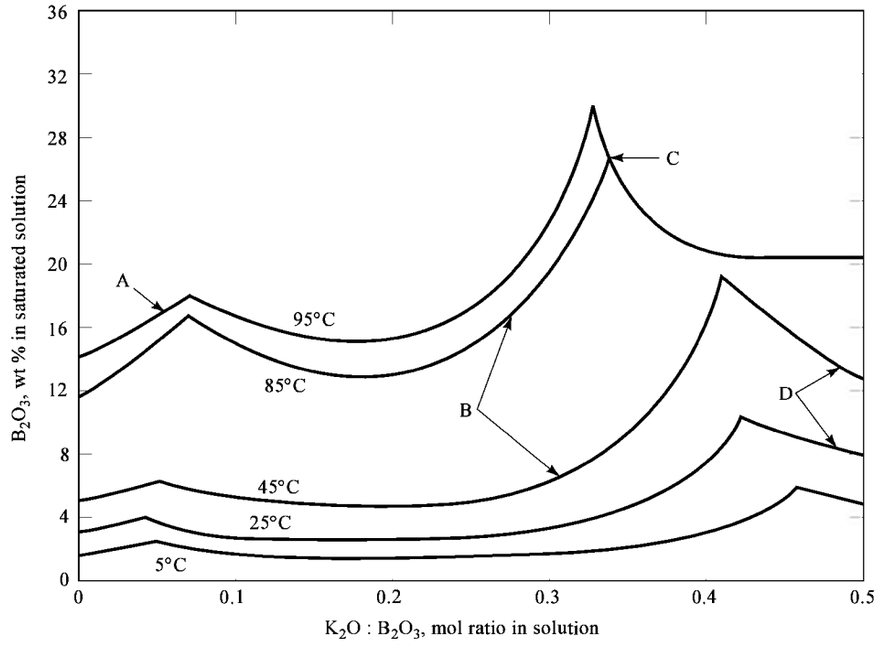


Fig. 8. Solubility isotherms for the $K_2O–B_2O_3–H_2O$ system at temperatures from 5 to 95°C where A, B, C, and D represent the solid phases $B(OH)_3$, $K_2O \cdot 5B_2O_3 \cdot 8H_2O$, $2K_2O \cdot 5B_2O_3 \cdot 5H_2O$, and $K_2O \cdot 2B_2O_3 \cdot 4H_2O$, respectively (120).

Single-crystal x-ray studies have shown that the borate ion in the potassium compound is identical to that found in borax (4) and has the structural formula $K_2[B_4O_5(OH)_4] \cdot 2H_2O$ (122).

Potassium Pentaborate Tetrahydrate. Potassium pentaborate tetrahydrate, $KB_5O_8 \cdot 4H_2O$ or $K_2O \cdot 5B_2O_3 \cdot 8H_2O$; formula wt, 293.20; orthorhombic prisms; sp gr, 1.74; heat capacity, 329.0 J (mol·K) [78.6 cal (mol·K)] at 296.6 K; is much less soluble than sodium pentaborate (Tables 9 and 10). Heat capacity measurements on the solid have been made over a broad temperature range (85).

The tetrahydrate is stable under normal conditions of storage. Its heat of dehydration has been calculated as 110.8 kJ mol (26.5 kcal mol) between 106.5 and 134°C (121). Its thermal stability is highly dependent on the partial pressure of atmospheric water. It is stable when heated in a vaccum up to 105°C; in an atmosphere saturated with water at 90°C, it is stable up to 170°C.

The solid-state structural formula is $K[B_5O(OH)_4] \cdot H_2O$ (123), which is analogous to that found in sodium pentaborate (5).

Diammonium Tetraborate Tetrahydrate. Diammonium tetraborate tetrahydrate, $(NH_4)_2B_4O_7 \cdot 4H_2O$ or $(NH_4)_2O \cdot 2B_2O_3 \cdot H_2O$; formula wt, 263.37; monoclinic; sp gr, 1.58; is readily soluble in water (Table 9). The pH of solutions of diammonium tetraborate tetrahydrate is 8.8 and independent of concentration. The compound is quite unstable and exhibits an appreciable vapor pressure of ammonia. Phase relationships have been outlined and the x-ray crystal structure formula is $(NH_4)_2[B_4O_5(OH)_4] \cdot 2H_2O$ (124).

Ammonium Pentaborate Tetrahydrate. Ammonium pentaborate tetrahydrate, $NH_4B_5O_8 \cdot 4H_2O$ or $(NH_4)_2O \cdot 5B_2O_3 \cdot 8H_2O$; formula wt, 272.13; sp gr, 1.567; heat capacity, 359.4 J (mol·K) [85.9 cal (mol·K)] at 301.2 K; exists in two crystalline forms, orthorhombic (α) and monoclinic (β). The α-form, which crystallizes as the kinetic product, is the commercial form of ammonium pentaborate tetrahydrate and the β-form is the thermodynamic product but is slow to crystallize. Its heat capacity has been measured over a broad temperature range (85). Solubility data are given in Table 9 and pH data in Table 10.

Ammonium pentaborate tetrahydrate is very stable in respect to ammonia loss. On heating from 100 to 230°C, it loses 75% of its water content but less than 1% of the ammonia. At 200°C, under reduced pressure, the water content drops to 1.15 mol, but only 2% of the ammonia is lost (61). At still higher temperatures all ammonia and water are expelled to give boric oxide (125).

The pentaborate is shown by x-ray data to contain the $[B_5O_6(OH)_4]^-$ ion (5), analogous to that found in the sodium and potassium compounds. The α-form has the structural formula $NH_4[B_5O(OH)_4] \cdot 2H_2O$ and the β-form $NH_4[B_5O_8] \cdot 4H_2O$ (126).

Lithium Borates. Two lithium borates are of minor commercial importance, the tetraborate trihydrate and metaborate hydrates.

Dilithium tetraborate trihydrate, $Li_2B_4O_7 \cdot 3H_2O$ or $Li_2O \cdot 2B_2O_3 \cdot 3H_2O$, has a density of 1.88 g mL. It crystallizes with difficulty from a supersaturated solution of lithium hydroxide and boric acid, which on standing forms a gelatinous deposit that is converted to hydrate crystals after boiling for several hours. The trihydrate is stable up to 180°C, then the compound dehydrates becoming anhydrous up to about 320°C, and fuses at 890°C.

Lithium metaborate octahydrate, $LiBO_2 \cdot 8H_2O$ or $Li_2O \cdot B_2O_3 \cdot 16H_2O$, hexagonal; *d* 1.825 g mL; has the structural formula $Li[B(OH)_4] \cdot 6H_2O$ (127). On heating to 70°C six waters are lost; the last two waters are lost between 140 and 280°C (128).

The octahydrate is the stable solid phase in contact with its solution below 36.9°C. Above this temperature lithium metaborate dihydrate, $LiBO_2 \cdot 2H_2O$ or $Li_2O \cdot B_2O_3 \cdot 4H_2O$, becomes the stable solid phase. Dihydrate crystals are orthorhombic having a density of 1.825 g mL and a structural formula $Li[B(OH)_4]$. In solution above 150°C a hemihydrate, $LiBO_2 \cdot 1 2H_2O$, forms and the anhydrous salt crystallizes above 225°C.

Manufacture. Potassium tetraborate tetrahydrate may be prepared from an aqueous solution of KOH and boric acid having a B_2O_3:K_2O ratio of about 2 or by separation from a KCl–borax solution (129). Potassium pentaborate is prepared in a manner analogous to that used for the tetraborate, but the strong liquor has a B_2O_3:K_2O ratio near 5.

Ammonium tetraborate tetrahydrate is prepared by crystallization from an aqueous solution of boric acid and ammonia having a B_2O_3:$(NH_4)_2O$ ratio of 1.8:2.1. Ammonium pentaborate is similarly produced from an aqueous solution of boric acid and ammonia having a B_2O_3:$(NH_4)_2O$ ratio of 5. Supersaturated solutions are easily formed and the rate of crystallization is proportional to the extent of supersaturation (130). A process for the production

of ammonium pentaborate by precipitation from an aqueous ammonium chloride–borax mixture has been patented (131).

Economic Aspects. The potassium, lithium, and ammonium borates are low volume products. Annual production figures are in the range of hundreds of metric tons. Prices of these borates during 1985 and 1990 are given in Table 16.

Table 16. Prices for Potassium, Ammonium, and Lithium Borates[a]

Chemical	1985	1990
$K_2O \cdot B_2O_3 \cdot 4H_2O$	2420	2838
$K_2O \cdot 5B_2O_3 \cdot 8H_2O$	2222	2618
$(NH_4)_2O \cdot 2B_2O_3 \cdot 4H_2O$	1980	2310
$(NH_4)_2O \cdot 5B_5O_8 \cdot 8H_2O$	1650	1936
$LiBO_2$		31.60[b]
$LiBO_2 \cdot 2H_2O$		11.70[b]
$Li_2O \cdot 2B_2O_3 \cdot 4H_2O$		24.30[b]

[a] Prices in $ t, carload quantities (>36 t in 45.4 kg (100 lb) bags unless otherwise indicated (33).

[b] Prices are in $ kg, 227–907 kg (500–2000 lb) lots, Lithium Corporation of America, Bessemer City, N.C. (12).

Health and Safety. Little toxicological data are available on borates other than boric acid and borax. Most water-soluble borates have the same toxicological effects as borax when adjusted to account for differences in B_2O_3 content.

Uses. Dipotassium tetraborate tetrahydrate is used to replace borax in applications where an alkali metal borate is needed but sodium salts cannot be used or where a more soluble form is required. The potassium compound is used as a solvent for casein, as a constituent in welding fluxes, and a component in diazotype developer solutions. Potassium pentaborate tetrahydrate is used in fluxes for welding and brazing of stainless steels for nonferrous metals. Diammonium tetraborate tetrahydrate is used when a highly soluble borate is desired but alkali metals cannot be tolerated. It is used mostly as a neutralizing agent in the manufacture of urea–formaldehyde resins and as an ingredient in flameproofing formulations. Ammonium pentaborate tetrahydrate is used as a component of electrolytes for electrolytic capacitors, as an ingredient in flameproofing formulations, and in paper coatings.

Calcium-Containing Borates

Dicalcium Hexaborate Pentahydrate. Dicalcium hexaborate pentahydrate, $Ca_2B_6O_{11} \cdot 5H_2O$ or $2CaO \cdot 3B_2O_3 \cdot 5H_2O$; formula wt, 411.08; monoclinic; sp gr, 2.42; heat of formation, 3.469 kJ mol (0.83 kcal mol) (132); exists in nature as the mineral colemanite. Its solubility in water is about 0.1% at 25°C and 0.38% at 100°C. Heats of solution have been determined in HCl (132). Colemanite is slowly formed on heating saturated solutions of inyoite, $2CaO \cdot 3B_2O_3 \cdot 13H_2O$, or other higher hydrates. Colemanite decrepitates violently at 480°C losing all its water and forming an anhydrous very low bulk density powder (133).

The crystal structure of colemanite has been shown to contain $[B_3O_4(OH)_3]^{2n-}{}_n$ polyanion chains. The structural relationships between colemanite and the other minerals of the series $2CaO \cdot 3B_2O_3 \cdot nH_2O$ (n 1, 5, 7, 9, 13), and structural changes accompanying the ferroelectric transition of colemanite have been outlined (134).

Sodium Calcium Pentaborate Octahydrate. Sodium calcium pentaborate octahydrate, $NaCaB_5O_9 \cdot 8H_2O$ or $Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 16H_2O$; formula wt, 405.23; triclinic; sp gr, 1.95; exists in nature as the mineral ulexite. The compound can be prepared by seeding a solution of 110 g $CaB_2O_4 \cdot 6H_2O$, 40 g boric acid, 100 g borax, 450 g $CaCl_2$ and 2.5 L H_2O (111). Ulexite is slowly converted to $NaCaB_5O_9 \cdot 5H_2O$, probertite, when seed is added to a moistened sample at 80–100°C. When crystals of ulexite are heated, four moles of water are lost at 80–100°C, 8.5 more until 175°C, and the remaining 3.5 on heating to 450°C (135).

The x-ray crystal structure consists of isolated pentaborate polyanions and the structural formula is $NaCa[B_5O_8(OH)_4] \cdot 5H_2O$ (136). Some specimens of ulexite have fiber optic properties with surprisingly good resolution of projected images. The fiber is aligned along the c-axis with index of 1.529. Cladding results from random orientation of crystals about the fiber direction, producing a core-to-cladding index difference ranging from 0 to a maximum of γ α 0.038 (137).

The solubility in water at 25°C is 0.5% as $NaCaB_5O_9$. Calcining at 200–500°C increases its solubility to 9–13 g L.

Sodium Calcium Pentaborate Pentahydrate. Sodium calcium pentaborate pentahydrate, $NaCaB_5O_9 \cdot 5H_2O$ or $Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 10H_2O$; formula wt 351.19; monoclinic; sp gr, 2.14; exists in nature as the mineral probertite. Probertite can be prepared by heating a mixture of two parts ulexite and one part borax to about 60°C (138) or by heating a borax and calcium metaborate solution at 105°C for eight days (74). The structural formula $NaCa[B_5O_7(OH)_4] \cdot 3H_2O$ has been determined from the crystal structure (139). By thermogravimetric analysis two moles of water are lost at 100°C, four more from 100° to 180°C, and slow loss of the last four up to 400°C.

Manufacture. The alkaline-earth metal borates of primary commercial importance are colemanite and ulexite. Both of these borates are sold as impure ore concentrates from Turkey, which is the principal world supplier. Colemanite and ulexite mining areas in Turkey are the Bigadic, Emet, and Kestelek regions. In 1986 Etibank run-of-mine production was about 793,000 t yr of colemanite and 185,000 t yr of ulexite. The concentrates produced are glass-grade material. The mining is both open-pit and underground.

At Hisarcik, in the Emet District, Etibank operates an open-pit mine and a colemanite concentrating plant. The production from this plant is relatively high in arsenic, about 3500 ppm. The ore consists of colemanite nodules, closely packed with shale. The presence of high concentrations of arsenic sulfides has been indicated. Plant capacity is about 184,000 t yr as B_2O_3. At Espey, Etibank operates an underground mine, which was to be converted to an open-pit mine, that had a capacity of 25,000 t yr as B_2O_3. A concentrating plant at Bigadic has a capacity of 132,000 t yr as B_2O_3 (6,140).

Death Valley, California, has historically been a significant source of both colemanite and ulexite, but mining in the Death Valley National Monument has been forbidden as a result of environmental concerns. In 1986, the American Borate Co. ceased mining in Death Valley, but continues to market ore concentrate from inventory as well as borates and concentrates imported from Turkey.

Specifications and Shipping. The colemanite, which is to be used in the production of glass fibers, must conform to the purchasers' specifications on Fe and As. Colemanite is available in bags and bulk.

Uses. Colemanite, $2CaO \cdot 3B_2O_3 \cdot 5H_2O$, is used in the production of boric acid and borax, as well as in several direct applications. It is a highly desirable material for the manufacture of the E-glass used in textile glass fibers and plastic reinforcement (where sodium cannot be tolerated). High As or Fe levels in the ore concentrate can limit its use in this application. Colemanite has seen limited application as a slagging material in steel manufacture. It is also used in some fire retardants and as a precursor to some boron alloys.

Ulexite, $NaCaB_5O_9 \cdot 8H_2O$, and probertite, $NaCaB_5O_9 \cdot 5H_2O$, have found application in the production of insulation fiber glass and borosilicate glass as well as in the manufacture of other borates.

Borate Melts and Glasses. Like silicon oxide and lead oxide, boric oxide (B_2O_3) is a natural glass network-forming oxide having very strong covalent bonds. These glass-forming oxides are capable of existing in the vitreous state either alone or in combination with other oxides. When heated alkali metal oxides, hydroxides, or carbonates fuse with boric acid or hydrated alkali metal borates to form a clear liquid melt. If these liquids are high

(M_2O B_2O_3 from 0 to 2 mol) in boric oxide content, they become viscous on cooling and form glasses.

Most of the interest in alkali metal borate glasses has centered on reports indicating the existence of maxima and minima in some of the physical properties of the glasses, such as viscosity, density, and thermal expansion coefficient, that occur with increasing metal oxide content. This phenomenon has been called the boron oxide anomaly (141). Modern theory on borate glass structure, however, indicates that these property changes are not anomalous but are the result of well-defined structural changes in the glass at the molecular level. Four different borate structural groups have been theorized to be present in alkali borate glasses below 34 mol % M_2O (142). These groups are shown in Figure 9. The triborate and pentaborate groups always occur in pairs which are then referred to as tetraborate groups. The argument that pure vitreous B_2O_3 consists of flat BO_3 triangles in the form of boroxol rings connected by BO_3 chains is strongly supported by boron nuclear quadrapole resonance spectroscopy (143). Addition of alkali oxide to boron oxide to form an alkali borate glass results in transformation of BO_3 triangles to BO_4 tetrahedra in a continuous manner. On addition of M_2O, up to 20 mol %, tetraborate groups are formed. Between 20 and 34 mol % M_2O, diborate groups form at the expense of the tetraborate groups. Infrared (142) and laser Raman (28) data on borate glasses and the analogous crystalline anhydrous borates support this reasoning. Changes in the physical properties of the glass with M_2O content represent compromises between the effect of adding more metal ions to the system and the effect of making the borate structural entities more rigid by converting trigonally coordinated borons to tetrahedrally coordinated borons.

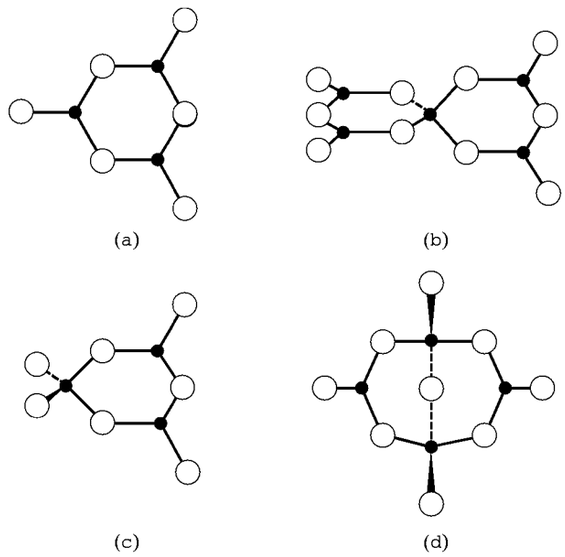


Fig. 9. The borate glass structural groups where ● boron; ○ oxygen; (**a**) boroxol; (**b**) pentaborate; (**c**) triborate; and (**d**) diborate (142).

Another widely studied phenomenon in alkali borate glasses is the mixed alkali effect, the nonlinear change in glass properties when a second kind of alkali oxide is added into the single-alkali glass. Models have been suggested to explain the mixed alkali effect (144), but a universally accepted model has not been developed as of this writing.

A number of reviews have appeared covering the various aspects of borate glasses. The structure, physical properties, thermochemistry, reactions, phase equilibria, and electrical properties of alkali borate melts and glasses have been presented (73). The application of x-ray diffraction, nmr, Raman scattering, ir spectroscopy, and esr to structural analysis is available (26). Phase-equilibrium diagrams for a large number of anhydrous borate systems are included in a compilation (145), and thermochemical data on the anhydrous alkali metal borates have been compiled (17).

The largest single commercial use of borates is in fiber glass. There are two basic types of glass fibers: insulation (soda lime borosilicate glass) and textile (low alkali lime aluminosilicate glass) grades. Borax pentahydrate is the most common source of B_2O_3 for making insulation fiber glass. Textile or E-glass fiber requires low sodium formulations and for this reason boric acid or colemanite is commonly used. Only borates having low arsenic content are suitable for use in glass making. Smaller amounts of borates are consumed in heat-resisting (Pyrex or low thermal expansion) glass, sealing glass, glazes and enamels (frit), optical glass, nuclear waste storage glass, and in the making of vycor. The typical range of B_2O_3 content in commercial glasses is shown in Table 17. Borates are not generally used in container or flat glass.

Table 17. Borate Content in Commercial Glass

Glass type	B_2O_3, wt %
fiber	
textile	6–13
insulation	3–7
heat resisting (pyrex)	12–15
sealing glass	8–30
porcelain enamel (frit)	11–13
vycor	20[a]

[a] This is the percent B_2O_3 in glass prior to acid leaching to form vycor.

Boron oxide, B_2O_3, can be added to a glass formulation from a variety of boron-containing compounds, but because the boron is taken into vitreous solution, it is often immaterial which source of boron is used. The choice of raw material is usually determined by consideration of the price per contained B_2O_3 unit, uniformity of composition, purity, hydration state, and compatibility of the cation in the finished glass. In addition, boron-containing raw materials are usually the only water-containing constituents in a glass batch and because the water must be removed in the melting furnace, the dehydration characteristics are important (144).

Boron oxide is added to borosilicate glass formulations to improve properties both in the finished glass and in the glass-making process (146). The benefits of B_2O_3 use in glass making are (*1*) creation of a low melting flux to dissolve refractory silica; (*2*) a lower liquidus temperature and inhibition of devitrification; (*3*) lower melt viscosity; (*4*) enhanced melt rate; and (*5*) improved draw qualities in fiber production. The benefits of B_2O_3 in the finished glass product are (*1*) improved chemical durability; (*2*) lower thermal expansion; (*3*) increased mechanical strength; (*4*) decreased devitrification tendency;

(*5*) improved scratching hardness; and (*6*) enhanced refraction, color, and brilliance.

Other Metal Borates

Borate salts or complexes of virtually every metal have been prepared. For most metals, a series of hydrated and anhydrous compounds may be obtained by varying the starting materials and or reaction conditions. Some have achieved commercial importance.

In general, hydrated borates of heavy metals are prepared by mixing aqueous solutions or suspensions of the metal oxides, sulfates, or halides and boric acid or alkali metal borates such as borax. The precipitates formed from basic solutions are often sparingly-soluble amorphous solids having variable compositions. Crystalline products are generally obtained from slightly acidic solutions.

Anhydrous metal borates may be prepared by heating the hydrated salts to 300–500°C, or by direct fusion of the metal oxide with boric acid or B_2O_3. Many binary and tertiary anhydrous systems containing B_2O_3 form vitreous phases over certain ranges of composition (145).

Barium Metaborate. Three hydrates of barium metaborate, $BaO \cdot B_2O_3 \cdot xH_2O$, are known. The tetrahydrate (147) and pentahydrate (148) both contain the $B(OH)_4^-$ anion, and are properly formulated as $Ba[B(OH)_4]_2 \cdot xH_2O$, where x 0 or 1. These compounds crystallize when solutions of barium chloride and sodium metaborate are combined at room temperature (149). The higher hydrate is favored when excess sodium metaborate is used. Saturated aqueous solutions contain 13.5 g L of $BaO \cdot B_2O_3 \cdot 4H_2O$ at 25°C. Both forms dehydrate at temperatures above 140°C (150). Barium metaborate may also be prepared from barium sulfide formed by prior reduction of barium sulfate. The presence of sulfide impurities in the product may render it unsuitable for some applications (61). Crystals of a hydrate, x 1.67 H_2O, form from a boiling solution having the B:Ba molar ratio <2. Dehydration of this hydrate at 300°C gives $BaO \cdot B_2O_3$ in which boron atoms are both triangularly and tetrahedrally coordinated (151).

Barium metaborate is used as an additive to impart fire-retardant and mildew-resistant properties to latex paints, plastics, textiles, and paper products (6). Barium metaborate is marketed by Buckman Labs, Inc., Memphis, Tennessee (12).

Copper, Manganese, and Cobalt Borates. Borate salts of copper, manganese, and cobalt are precipitated when borax is added to aqueous solutions of the metal(II) sulfates or chlorides (152). However, these materials are no longer produced commercially.

Zinc Borates. A series of hydrated zinc borates have been developed for use as fire-retardant additives in coatings and polymers (59,153). Worldwide consumption of these zinc salts is several thousand metric tons per year. A substantial portion of this total is used in vinyl plastics where zinc borates are added alone or in combination with other fire retardants such as antimony oxide or alumina trihydrate.

Zinc borate $2ZnO \cdot 3B_2O_3 \cdot 7H_2O$ is formed when borax is added to aqueous solutions of soluble zinc salts at temperatures below about 70°C. An x-ray structure determination has indicated that this compound is orthorhombic and has a zinc triborate monohydrate structure, $Zn[B_3O_3(OH)_5] \cdot H_2O$ (2). Zinc borates $2ZnO \cdot 3B_2O_3 \cdot 7H_2O$ and $ZnO \cdot B_2O_3 \cdot 2H_2O$ lose water of hydration when heated from 130 to 250°C (59).

A different crystalline hydrate, $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$, equivalent to $4ZnO \cdot 6B_2O_3 \cdot 7H_2O$, is produced when the reaction between zinc oxide and boric acid is carried out at temperatures of 90–100°C (154). This product has also been crystallized from solutions containing borax, zinc chloride, and sodium hydroxide (155). It is marketed by the United States Borax & Chemical Corp. under the trademark FIREBRAKE ZB, BOROGARD ZB, and under AMAX, Inc. as ZB-467. This compound has the unusual property of retaining its water of hydration at temperatures up to 290°C. This thermal stability makes it attractive as a fireretardant additive for plastics and rubbers that require high processing temperatures. It is also used as an anticorrosive pigment in coatings. The 1990 selling price for FIREBRAKE ZB ranged from $2.40 kg to $2.90 kg (12). Zinc borates are also manufactured by Storey (UK) and Waardals (Norway).

Zinc borate $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ has an acute oral toxicity in rats LD_{50} > 10,000 mg kg body weight and acute dermal toxicity in rabbits LD_{50} > 10,000 mg kg body weight. It is not a skin irritant and gives a negative response in the Ames mutagenicity test.

Boron Phosphate

Boron phosphate, BPO_4, is a white, infusible solid that vaporizes slowly above 1450°C, without apparent decomposition. It is normally prepared by dehydrating mixtures of boric acid and phosphoric acid at temperatures up to 1200°C.

$$B(OH)_3 + H_3PO_4 \rightarrow BPO_4 + 3\,H_2O$$

Complete dehydration requires temperatures above 1000°C.

The structure of boron phosphate prepared under normal atmospheric conditions consists of tetragonal bipyrimids analogous to the high cristobalite form of silica. Both the boron and phosphorus are tetrahedrally coordinated by oxygen. Similar silicalike structures are found for $BAsO_4$ and $TaBO_4$ (156). A quartzlike form of boron phosphate can be prepared by heating the common form to 500°C at 5.07 GPa (50,000 atm) (157).

The tri-, tetra-, penta-, and hexahydrates of boron phosphate have been reported. All of these decompose rapidly in water to give solutions of the parent acids. Anhydrous boron phosphate hydrolyzes in a similar fashion, though the reaction proceeds quite slowly for material that has been ignited at high temperatures.

The principal application of boron phosphate has been as a heterogeneous acid catalyst (158).

Although boron phosphate is derived from two of the three most common glass-forming oxides, it exhibits little tendency to form a glass itself. Boron phosphate is a primary phase over a considerable portion of the B_2O_3–SiO_2–P_2O_5 system (159).

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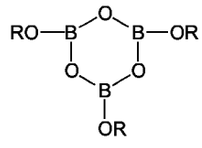
BORIC ACID ESTERS

In 1846 the first boric acid esters were prepared by reacting aliphatic alcohols and boron trichloride (1). The chemistry and properties of boric acid esters from that first paper through 1961 have been extensively reviewed (2). Short reviews were published in 1964, 1978, and two in 1980 (3,4).

The general formula for boric acid esters is $B(OR)_3$. The lower molecular weight esters such as methyl, ethyl, and phenyl are most commonly referred to as methyl borate *[121-43-7]*, ethyl borate *[150-46-9]*, and phenyl borate *[1095-03-0]*, respectively. Some of the most common boric acid esters used in industrial applications are listed in Table 1. The nomenclature in the boric acid ester series can be confusing. The IUPAC committee on boron chemistry has suggested using trialkoxy- and triaryloxyboranes (5) for compounds usually referred to as boric acid esters, trialkyl (or aryl) borates, trialkyl (or aryl) orthoborates, alkyl (or aryl) borates, alkyl (or aryl) orthoborates, and in the older literature as boron alkoxides and aryloxides. Cyclic boric acid esters, which are trimeric derivatives of metaboric acid (HBO_2), are known as boroxines (1).



(1)

Table 1. Properties of Boric Acid Ester Derivatives

Compound name	CAS Registry Number	Molecular formula	Mp, °C	Bp, °C[a]	d_4^t	n_D[b]
trimethyl borate	*[121-43-7]*	$B(OCH_3)_3$	29	68.0–68.5	0.920^{20}	1.3548
trimethyl borate azeotrope		$B(OCH_3)_3 \cdot CH_3OH$		54.3	0.8804^{25}	1.3472
triethyl borate	*[150-46-9]*	$B(OCH_2CH_3)_3$	84.8	117–119	0.859^{2}	1.3723
triethyl borate azeotrope		$B(OCH_2CH_3)_3 \cdot 7.75CH_3CH_2OH$		76.6		
tri-*n*-propyl borate	*[688-71-1]*	$B(OCH_2CH_2CH_3)_3$		176–179	0.356^{24}	1.3933
triisopropyl borate	*[5419-55-6]*	$B[OCH(CH_3)_2]_3$		139–140	0.815^{23}	1.3750
tri-*n*-butyl borate	*[688-74-4]*	$B(OCH_2CH_2CH_2CH_3)_3$		227	0.856^{25}	1.4077
triphenyl borate	*[1095-03-0]*	$B(OC_6H_5)_3$	80–90[c]	360–370 224–230[d]		
tricresyl borate[e]	*[26248-41-9]*	$B(OC_6H_4CH_3)_3$		185–200[f]		
trimethoxyboroxine (**1**, R = CH_3)	*[102-24-9]*	$C_3H_9B_3O$		dec	1.2286^{25}	
triisopropoxyboroxine (**1**, R = *i*-$CH_7$3)	*[10298-87-0]*	$C_9H_{21}B_3O$	52–54	235–239 dec		
2,2′-oxybis[4,4,6-trimethyl-1,3,2-dioxaborinane] (2)	*[1497-50-8]*			114–115[f]	1.013^{24}	1.4308
2,2′-[1-methyl-1,3-propanediyl]bis(oxy)-bis[4-methyl-1,3,2-dioxaborinane] (3)	*[2665-13-6]*	$C_{12}H_{24}B_2O$		207–213[d]	1.071^{25}	1.4464[g]
	[26545-48-2]	$C_{18}H_{40}B_2O_8$		274–276	0.932^{21}	1.4381
2,2′-[1,1,3-trimethyltrimethylene-dioxy]bis[4,4,6-trimethyl-1,3,2-dioxaborinane] (4)				170–172[h]		
triethanolamineborate	*[283-56-7]*	$B(OCH_2CH_2)_3N$	235–239			

[a] At 101.3 kPa (760 mm Hg) unless otherwise indicated.

[b] At 25°C unless otherwise indicated.

[c] Triphenyl borate has been reported to melt at temperatures from 38 to 146°C. Most values are in the range of 80–90°C.

[d] At 2.3 kPa (17 mm Hg).

[e] Mixture of the m- and p-isomers.

[f] At 0.27 kPa (2 mm Hg).

[g] At 17°C.

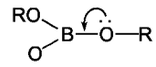
[h] At 2.7 kPa (20 mm Hg).

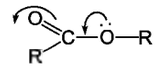
Physical Properties

Most reported boric acid esters are trialkoxy or triaryloxy boranes. The esters range from colorless low boiling liquids to solids that possess high melting points. Boric acid esters usually have an odor similar to the hydroxy compound from which they are derived. A more complete description of the physical

properties of the compounds, given in Table 1, has been published (2). The density and viscosity (6), surface tension (7), vapor pressure, and other thermodynamic data (8,9) of a number of common boric acid esters have been summarized. In addition, information on the dipole moments of boric acid esters has been published (10).

The trialkoxy(aryloxy)boranes are typically monomeric, soluble in most organic solvents, and dissolve in water with hydrolysis to form boric acid and the corresponding alcohol and phenol. Although the rate of hydrolysis is usually very fast, it is dependent on the bulk of the alkyl or aryl substituent groups bonded to the boron atom. Secondary and tertiary alkyl esters are generally more stable than the primary alkyl esters. The boron atom in these compounds is in a trigonal coplanar state with sp^2 bond hybridization. A vacant *p* orbital exists along the threefold axis perpendicular to the BO_3 plane. This vacant *p* orbital readily accepts adjacent unshared electrons, electronically acting in a manner similar to the carbonyl group of an organic ester.





This comparison is further demonstrated by observing that the chemistry of both trigonal boron and carbonyl carbon are strongly influenced by the ready acceptance of attacking nucleophiles.

$$H_3BO_3 + 3\,ROH \rightleftharpoons (RO)_3B + 3\,H_2O \tag{1}$$

$$R'COOH + ROH \rightleftharpoons R'COOR + H_2O \tag{2}$$

Chemical Properties

Alkyl boric acid esters derived from straight-chain alcohols and aryl boric acid esters are stable to relatively high temperatures. Methyl borate is stable to 470°C (11). Trialkoxyboranes from branched-chain alcohols are much less stable, and boranes from tertiary alcohols can even decompose at 100°C (12). Decomposition of branched-chain esters leads to mixtures of olefins, alcohols, and other derivatives.

Boric acid esters are very susceptible to hydrolysis in the presence of water, or in some cases atmospheric moisture. Partially hydrolyzed derivatives such as $(RO)_2BOH$ have not been isolated except in special cases involving large substituent groups. The comparative hydrolysis rates for a number of borate esters has been reported (13). When borate esters are hydrolyzed, the boron atom is transformed from an sp^2 trigonal coplanar configuration in the ester to an sp^3 hybridization in a tetrahedral intermediate. Therefore, the most obvious rate-determining factors in the transformation are the steric requirements of the tetrahedral species. Tri-*n*-propanolamine borate is somewhat stable, presumably because of the compactness of the transannular form that completely precludes the inversion to the necessary tetrahedral configuration on entry of water. Most hydrolytically stable derivatives contain bulky alcohol or phenolic groups dispersed both above and below the BO_3 plane. Some particularly stable examples are tri-*t*-amyl borate *[22238-22-8]*, $C_{15}H_{33}BO_3$, tri-2-cyclohexylcyclohexyl borate *[5440-19-7]*, $C_{3}H_{3}BO_3$, and the general class of hindered phenolic borates. Borate esters, in which the boron atom is coordinated through its vacant orbital with an internal nitrogen atom containing a free electron pair, also exhibit good hydrolytic stability. Two examples are triethanolamine borate and triisopropylamine borate *[101-00-8]*, $C_9H_{18}BNO_3$. Nuclear magnetic resonance (nmr) (14) and infra red (ir) spectroscopy (15,16), as well as mass spectrometry (16,17) have been used to help elucidate the structures of various borate esters.

Preparative Methods

There are a number of methods used for the preparation of borate esters.

From Boric Acid. The most common method for the preparation of trialkoxy- and triaryloxyboranes is the esterification of boric acid using three moles of an alcohol or phenol.

$$B(OH)_3 + 3\,ROH \rightleftharpoons B(OR)_3 + 3\,H_2O \tag{3}$$

The equilibrium shown in equation 3 normally lies far to the left. Usually the water formed is removed by azeotropic distillation with excess alcohol or a suitable azeotroping solvent such as benzene, toluene, or various petroleum distillate fractions. The procedure used depends on the specific ester desired. Preparation of methyl borate and ethyl borate is complicated by the formation of low boiling azeotropes (Table 1) which are the lowest boiling constituents in these systems. Consequently, the ester–alcohol azeotrope must be prepared and then separated in another step. Some of the methods that have been used to separate methyl borate from the azeotrope are extraction with sulfuric acid and distillation of the enriched phase (18), treatment with calcium chloride or lithium chloride (19,20), washing with a hydrocarbon and distillation (21), fractional distillation at 709 kPa (7 atmospheres) (22), and addition of a third component that will form a low boiling methanol azeotrope (23).

From Boric Oxide and Alcohol. To avoid removing water, boric oxide, B_2O_3, can be used in place of boric acid. The water of reaction (eq. 4) is consumed by the oxide (eq. 5). Because boric acid reacts with borates at high temperatures, it is necessary to filter the reaction mixture prior to distillation of the product. Only 50% of the boron can be converted to ester by this method. In cases where this loss can be tolerated, the boric oxide method is convenient. This is particularly true for methyl borate and ethyl borate preparation because formation of the undesirable azeotrope is avoided.

$$\frac{1}{2}B_2O_3 + 3\,ROH \rightarrow B(OR)_3 + \frac{3}{2}H_2O \tag{4}$$

$$\frac{1}{2}B_2O_3 + 3\,H_2O \rightarrow 2\,B(OH)_3 \tag{5}$$

The esterification of boric oxide does not require the removal of water. However, if high yields based on boron are desired, six or more moles of alcohol must be used and the water must be removed.

$$B_2O_3 + 6\,ROH \rightarrow 2\,B(OR)_3 + 3\,H_2O \tag{6}$$

The rate of ester production is dependent on the removal of water (or ester) from the reaction, and consequently on the azeotroping agent used. The rate of ester production is greater using boric oxide than using boric acid and a given azeotroping agent.

Transesterification. Transesterification is another method that does not require the removal of water. If a borate of lower molecular weight is available, higher molecular weight esters may be prepared by reaction of the appropriate higher molecular weight alcohol.

$$B(OR)_3 + 3\,R'OH \rightleftharpoons B(OR')_3 + 3\,ROH \tag{7}$$

The liberated alcohol must be lower boiling than any other species present so that it may be distilled at a convenient rate and drive the reaction to completion. It is possible to prepare esters of lower molecular weight from a higher member by using a large excess of alcohol and rapid inefficient distillation, but the method is generally not practical.

Steric factors are important in transesterification reactions. With a given alcohol, primary alkyl borates react at a rate too fast to measure, secondary alkyl borates react at measurable rates, and *tert*-butyl borate reacts very slowly.

A continuous process has been developed for preparing borate esters using transesterification (24). Another modification of this method has been reported where use of molecular sieves (qv) to absorb the low boiling alcohol is used rather than distillation (25).

From Boron Halides. Using boron halides is not economically desirable because boron halides are made from boric acid. However, this method does provide a convenient laboratory synthesis of boric acid esters. The esterification of boron halides with alcohol is analogous to the classical conversion of carboxylic acid halides to carboxylic esters. Simple mixing of the reactants at room temperature or below in a solvent such as methylene chloride, chloroform, pentane, etc, yields hydrogen halide and the borate in high yield.

$$BCl_3 + 3\,ROH \rightarrow (RO)_3B + 3\,HCl \tag{8}$$

The reaction is irreversible and can be used to synthesize aliphatic and aromatic esters. In addition, there are no complications involving water removal or azeotrope formation. Boron tribromide can be used in place of boron trichloride, but the bromide has a stronger tendency to halogenate the alkyl group of the alcohol (26). Boron trifluoride does not give the ester, but gives either a complex or dehydrated product.

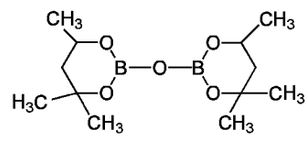
Miscellaneous Methods. Other methods for preparing borate esters have also been described (2,3). These include alcoholysis of borax or other alkali metal borates in either neutral or acidic media, disproportionation, decomposition or reaction of alkoxyhaloboranes, and disproportionation of trialkoxyboroxines. A simple and convenient method for synthesizing trialkoxyboranes and trialkoxyboroxines using calcium hydride as a drying agent has been published (27). It is claimed that a variety of borate esters containing sterically hindered alcohols can be prepared by using this procedure.

Manufacture and Economic Aspects

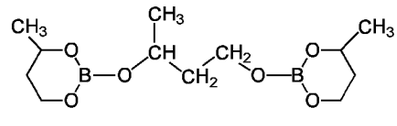
There are relatively few producers of boric acid esters in the United States. Eight domestic producers of these compounds (28) are: Anderson Development Co., Akzo America, Inc., E. I. du Pont de Nemours & Co., Inc., Eagle-Picher Industries, Inc., The Gas Flux Co., Morton International, Callery Chemical Co., and U.S. Borax & Chemical Corp. In addition, Rhone-Poulenc Chemicals, Manchester, UK, produces commercial quantities of selected boric acid esters.

Methyl borate is believed to be the boric acid ester produced in the largest quantity, approximately 8600 metric tons per year (28). Most methyl borate is produced by Morton International and used captively to manufacture sodium borohydride *[16940-66-2]*. Methyl borate production was studied in detail during the 1950s and 1960s when this compound was proposed as a key intermediate for production of high energy fuels. Methyl borate is sold as either the pure compound or as the methanol azeotrope that consists of approximately a 1:1 molar ratio of methanol to methyl borate.

A combination of the two dioxaborinanes, (2) and (3), is marketed as a fuel microbiocide by Hammonds Fuel Additives, Inc., Houston, Texas, under the trademark BIOBOR JF. Annual U.S. production and consumption is estimated at 140–230 metric tons (28).

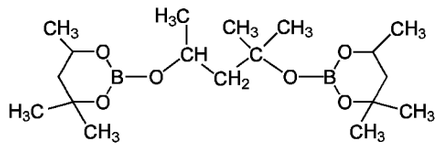


(2)



(3)

U.S. Borax Research Corp., Anaheim, California, markets several borate esters under the trademark BORESTER. These include triethanolamine borate (BORESTER 20), tricresyl borate (m- and p-isomers) (BORESTER 8), and the biborate (4) (BORESTER 7). Whereas the chemical name for (4) is given in Table 1, it is commonly referred to as trihexylene glycol biborate *[26545-48-2]* and is prepared by the reaction of two moles of boric acid and three moles of hexylene glycol.



(4)

Processes to produce boric acid esters are based on the azeotropic removal of water from a mixture of the appropriate alcohol, phenol, or glycol, and boric acid. A suitable hydrocarbon azeotroping agent is used to help remove the water. The water is removed continuously by using a condenser that allows continuous return of the solvent to the reaction vessel. For some borate esters, such as the glycol borates, distillation can result in decomposition. As a result the undistilled bottoms product is often used commercially. If further purification is necessary, these products can be vacuum distilled.

Prices for borate esters vary depending on the ester and the quantity. Whereas prices are usually between $3 and 9 kg, some esters are priced as high as $30–40 kg (28,29). U.S. imports and exports of the various boric acid esters is negligible (28).

Handling and Shipping

Procedures for shipping boric acid esters depend on the particular compound. Aryl borates produce phenols when in contact with water and are therefore subject to shipping regulations governing such materials and must carry a Corrosive Chemical label. Lower alkyl borates are flammable, flash points of methyl, ethyl, and butyl borates are 0, 32, and 94°C, respectively, and must be stored in approved areas. Other compounds are not hazardous, and may be shipped or stored in any convenient manner. Because borate esters are susceptible to hydrolysis, the more sensitive compounds should be stored and transferred in an inert atmosphere, such as nitrogen.

The usual containers for shipping are glass for small quantities, and steel cans, drums, or tank cars for bulk items. Over a period of time, moisture passes through the walls of some plastic containers. If this occurs, the more hydrolytically unstable borate esters may hydrolyze. Thus caution should be used when storing borate esters in plastic. In addition, shipping in metal cans or drums is not acceptable where hydrolysis can lead to a corrosive product, such as a halogenated alcohol.

Analytical and Test Methods

For the most part boric acid esters are quantitated by hydrolysis in hot water followed by determination of the amount of boron by the mannitol titration (see BORON COMPOUNDS, BORIC OXIDE, BORIC ACID AND BORATES). Separation of and measuring mixtures of borate esters can be difficult. Any water present causes hydrolysis and in mixtures, as a result of transesterification, it is possible to have a number of borate esters present. For some borate esters, such as triethanolamine borate, hydrolysis is sufficiently slow that quantitation by hydrolysis and titration cannot be done. In these cases, a sodium carbonate fusion is necessary.

Health and Safety

The toxicity of a few boric acid esters has been summarized (30). In general the toxicities are directly related to the toxicity of the alcohol or phenol produced on hydrolysis. Methyl borate has an oral rat LD_{50} of 6.14 mL kg in a range finding test (31) and the percutaneous LD_{50} for the rabbit of 1.98 mL kg. In earlier work (32), the oral LD_{50} for the rat was 2.82 mL kg; the intraperitoneal LD_{50} was 3.2 mL kg. It has been shown that the mouse is more susceptible to these compounds than the rat. Methyl borate was found to be moderately irritating in an ocular toxicity test using rabbits (31,32) but only mildly irritating to skin (31).

Uses

Production of Sodium Borohydride. In the pulp and paper industry, sodium borohydride is used to generate sodium hydrosulfite (sodium dithionite), a bleaching agent, from sodium bisulfite. Methyl borate is used as an intermediate in the production of sodium borohydride (33).

$$(CH_3O)_3B + 4\,NaH \rightarrow NaBH_4 + 3\,NaOCH_3 \tag{9}$$

Gas Fluxing. The methyl borate azeotrope is used as a gaseous flux for welding and brazing. The Gas Flux Co., Elyria, Ohio, manufactures the methyl borate azeotrope for their own use. The azeotrope acts as a volatile source of boric oxide and is introduced directly into the gas stream as a flux for the surfaces to be joined in the welding process. The European automobile industry is the primary user of this process, though there may be some usage for this purpose in the United States.

Polymer Additives. The addition of borate esters to polymers has been thoroughly investigated. Though the patent literature in this field has expanded, the actual usage of borate esters for this application is believed to be small. Studies have been done indicating that borate esters can be used as curing agents or hardeners in epoxy systems (see EPOXY RESINS). However, there is no indication that borate esters are being used in large quantities for this application. Some patents describing this application are given (34–39).

Borate esters have been used as antioxidants (qv) (40). Because of commercial inaccessibility and high cost their commercial use has not been extensive, although interest in this use does exist (41,42).

Hydraulic Fluids and Lubricants. The use of borate esters in hydraulic fluids (qv) and lubricants (see LUBRICATION AND LUBRICANTS) has been described in numerous patents (40,43,44). A variety of borate esters have been described that can be used as multifunctional lubricant additives having antiwear and antifriction properties (45).

Biocides. Many boric acid esters have been tested against microorganisms. BIOBOR JF is effective against microorganisms that contaminate hydrocarbon fuel. This product, which contains glycol borates (2) and (3), has been used successfully in jet fuels, heating oils, and various diesel applications. A variety of boric acid esters of various alcohols have been screened for antimicrobial activity in spent coolants of water-based cutting fluids. Some of the compounds tested showed good antimicrobial activity (46).

Hydrocarbon Oxidation. The oxidation of hydrocarbons (qv) and hydrocarbon derivatives can be significantly altered by boron compounds. Several large-scale commercial processes, such as the oxidation of cyclohexane to a cyclohexanol–cyclohexanone mixture in nylon manufacture, are based on boron compounds (see CYLCOHEXANOL AND CYCLOHEXANONE; FIBERS, POLYAMIDE). A number of patents have been issued on the use of borate esters and boroxines in hydrocarbon oxidation reactions, but commercial processes apparently use boric acid as the preferred boron source. The literature in this field has been covered through 1967 (47). Since that time the literature consists of foreign patents, but no significant applications have been reported for borate esters.

Miscellaneous Uses. Research has demonstrated that fabrics could be treated with vaporous trimethyl borate (70% azeotrope) resulting in textiles (qv) that are smoulder resistant (48).

Borates can be used as wood preservatives. Technology is being developed to treat wood (qv) with trimethyl borate in a vapor-treating process similar to that used for textiles (qv) (49). This method is based on impregnation using a preservative vapor. Gaseous trimethyl borate reacts with moisture in wood or wood products to form solid boric acid. The boric acid formed acts as a wood preservative preventing damage from wood-destroying fungi and insects. Shaped rods, pellets, or tablets composed of inorganic borates have also been used as wood preservatives. Borate esters have also been proposed for this use (50).

Isopropyl borate is used primarily in the production of catalysts for polyolefins and as an antiscratch agent for glass containers. *N*-Butyl borate is used as an adhesion promoter and had been used in fire retardant compositions.

Various borate esters are chemosterilants for house flies (51). Tributyl borate, available from Eagle-Picher, Miami, Oklahoma, which is isotopically enriched in boron-10, is being used as a chemical precursor in the synthesis of pharmacologically active boron compounds suitable for boron neutron capture therapy.

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REFRACTORY BORON COMPOUNDS

Borides have metallic characteristics such as high electrical conductivity and positive coefficients of electrical resistivity. Many of them, particularly the borides of metals of Groups 4 (IVB), 5 (VB), and 6 (VIB), the MB compounds of Groups 2(II) and 13(III), and the borides of aluminum and silicon, have high melting points, great hardness, low coefficients of thermal expansion, and good chemical stability.

Borides are inert toward nonoxidizing acids; however, a few, such as Be_2B and MgB_2, react with aqueous acids to form boron hydrides. Most borides dissolve in oxidizing acids such as nitric or hot sulfuric acid and they are also readily attacked by hot alkaline salt melts or fused alkali peroxides, forming the more stable borates. In dry air, where a protective oxide film can be preserved, borides are relatively resistant to oxidation. For example, the borides of vanadium, niobium, tantalum, molybdenum, and tungsten do not oxidize appreciably in air up to temperatures of 1000–1200°C. Zirconium and titanium borides are fairly resistant up to 1400°C. Engineering and other properties of refractory metal borides have been summarized (1).

Table 1 lists many metal borides and their observed melting points. Most metals form more than one boride phase and borides often form a continuous series of solid solutions with one another at elevated temperatures; thus close composition control is necessary to achieve particular properties. The relatively small size of boron atoms facilitates diffusion.

Table 1. Metal Borides[a]

Molecular formula	Boride	CAS Registry Number	Mp[b], °C	Molecular formula	Boride	CAS Registry Number	Mp[b], °C
AlB_2	aluminum diboride	*[12041-50-8]*	}0} $"⌠975, d	NdB	neodiymium hexaboride	*[12008-23-0]*	2540
AlB_{12}	aluminum boride (1:12)	*[12041-54-2]*	}} $"⌠2070	NiB	nickel boride	*[12007-00-0]*	1080
BaB	barium hexaboride	*[12046-08-1]*	}} $"⌠2070	Ni_2B	dinickel boride	*[12007-01-1]*	1230
BeB_2	beryllium diboride	*[12228-40-9]*	>1970	Ni_2B_2	dinickel diboride	*[12007-00-0]*	1160
BeB	beryllium hexaboride	*[12228-40-9]*	}} $"⌠2070	Ni_3B	trinickel boride	*[12007-02-2]*	1155
Be_2B	diberyllium boride	*[12536-51-5]*	}} $"⌠1520	Pd_3B	tripalladium boride	*[12429-53-7]*	820, d
Be_5B	pentaberyllium boride	*[12536-53-7]*	}} $"⌠1160	Pd_5B_2	pentapalladium diboride	*[11130-91-9]*	870, d
CaB	calcium hexaboride	*[12007-99-7]*	}} $"⌠2235	ReB_2	rhenium diboride	*[12355-99-6]*	2400
CeB	cerium boride	*[12045-00-0]*		RuB	ruthenium boride	*[12523-59-0]*	1600
CeB_4	cerium tetraboride	*[12007-52-2]*	}} $"⌠2380, d	RuB_2	ruthenium diboride	*[12360-00-8]*	1600, d
CeB	cerium hexaboride	*[12008-02-5]*	}0} $"⌠550	Ru_2B_3	dirutherium triboride	*[12356-00-2]*	1600
CoB	cobalt boride	*[12006-77-8]*	}} $"⌠1460	ScB_2	scandium diboride	*[12007-34-0]*	2250
Co_2B	dicobalt boride	*[12045-01-1]*	}} $"⌠1285	ScB	scandium hexaboride	*[12785-49-8]*	
Co_3B	tricobalt boride	*[12006-78-9]*	}} $"⌠1125, d	SiB_4	silicon tetraboride	*[12007-81-7]*	1870, d
CrB	chromium boride	*[12006-79-0]*	}} $"⌠2060	SiB	silicon hexaboride	*[12008-30-9]*	1980, d
CrB_2	chromium diboride	*[12007-16-8]*	}} $"⌠2130	SmB_4	samarium tetraboride	*[12007-82-8]*	
Cr_2B	dichromium boride	*[12006-80-3]*	}} $"⌠1875	SmB	samarium hexaboride	*[12008-29-6]*	2540
Cr_3B_2	trichromium diboride	*[12045-40-8]*	}} $"⌠1960	SrB	strontium hexaboride	*[12046-08-1]*	2235
Cr_3B_4	trichromium tetraboride	*[12045-71-5]*	}} $"⌠1920	TaB	tantalum boride	*[12007-07-7]*	2040
Cr_4B	tetrachromium boride	*[12006-81-4]*	}} $"⌠1680	TaB_2	tantalum diboride	*[12007-35-1]*	3100
FeB	iron boride	*[12006-84-7]*	≈1550	Ta_2B	ditantalum boride	*[12045-26-0]*	1900
Fe_2B	diiron boride	*[12006-86-9]*	}} $"⌠1390	Ta_3B_4	tritantalum tetraboride	*[12045-92-0]*	2650
				Ta_3B_2	tritantalum diboride	*[12045-92-0]*	2450
GdB_4	gadolinium tetraboride	*[12007-54-4]*		ThB_4	thorium tetraboride	*[12007-83-9]*	2500
GdB	gadolinium hexaboride	*[12008-06-9]*	}} $"⌠2100	ThB	thorium hexaboride	*[12229-63-9]*	2195
HfB	hafnium boride	*[12228-27-2]*	}} $"⌠2100, d	TiB	titanium boride	*[12007-08-8]*	2600

HfB_2	hafnium diboride	*[12007-23-7]*	}} $" ~3250	TiB_2	titanium diboride	*[12045-63-5]*	2900 ± 50
LaB_4	lanthanum tetraboride	*[12007-73-7]*	}} $" ~1800	Ti_2B	dititanium boride	*[12305-68-9]*	2200
LaB	lanthanum hexaboride	*[12008-21-8]*	}} $" ~2150	Ti_2B_5	dititanium pentaboride	*[12447-59-5]*	2670
MgB_2	magnesium diboride	*[12007-25-9]*	}0} $" ~800, d	UB_2	uranium diboride	*[12007-36-2]*	2385
MgB	magnesium hexaboride	*[12008-22-9]*	}} $" ~1100, d	UB_4	uranium tetraboride	*[12007-84-0]*	2495
MgB_{12}	magnesium boride (1:12)	*[12230-32-9]*	}} $" ~1300, d	UB	uranium hexaboride		2235
MnB	manganese boride	*[12045-15-7]*	}} $" ~1890	VB	vanadium boride	*[12045-27-1]*	2250
MnB_2	manganese diboride	*[12228-50-1]*	}} $" ~1900	VB_2	vanadium diboride	*[12007-77-3]*	2450
MnB_4	manganese tetraboride	*[12271-96-4]*	}} $" ~2160	V_2B_3	divanadium triboride	*[12313-74-5]*	2300
Mn_2B	dimanganese boride	*[12045-16-8]*	}} $" ~1580	V_3B_2	trivanadium diboride	*[12421-53-3]*	2060
Mn_3B_4	trimanganese tetraboride	*[12229-02-6]*	}} $" ~1750, d	WB	tungsten boride	*[12007-09-9]*	2660
Mn_4B	tetramanganese boride	*[12260-22-9]*	}} $" ~1285, d	W_2B	ditungsten boride	*[12007-10-2]*	2670
MoB	molybdenum boride	*[12006-98-3]*	}0} $" ~600	W_2B_5	ditungsten pentaboride	*[12007-98-6]*	2365
MoB_2	molybdenum diboride	*[12007-27-1]*	}} $" ~2300, d	YB_2	yttrium diboride	*[12429-58-2]*	2100
Mo_2B	dimolybdenum boride	*[12006-99-4]*	}} $" ~2280	YB_4	yttrium tetraboride	*[12045-95-3]*	2800
Mo_2B_2	dimolybdenum diboride	*[12006-98-3]*	}} $" ~2066	YB	yttrium hexaboride	*[12008-32-1]*	2600, d
Mo_2B_5	dimolybdenum pentaboride	*[12007-97-5]*	}} $" ~2100	YB_{12}	yttrium boride (1:12)	*[12046-90-1]*	2200, d
NbB	niobium boride	*[12045-19-1]*	}} $" ~2270	ZrB	zirconium boride	*[12045-28-2]*	2800
NbB_2	niobium diboride	*[12007-29-3]*	}} $" ~2900	ZrB_2	zirconium diboride	*[12045-64-6]*	3040
				ZrB_{12}	zirconium boride (1:12)	*[12046-91-2]*	2250, d

[a] Ref. 2.

[b] d Decomposes.

The structures of borides range from the isolated boron atoms in the M_2B borides through single chains in MB borides, double chains (M_3B_4), two-dimensional hexagonal nets (MB_2), cross-linked nets (MB_4), and interconnected B octahedra (MB), to cages of 24 boron atoms surrounding the central metal atom in the MB_{12} borides (3,4). The three-dimensional frameworks of the boron-rich borides provide stable lattices through which the metal atoms may migrate at high temperatures, ca 1600°C; damaged surfaces may thereby be rejuvenated. These stable lattices also improve the chemical stability of such borides.

Preparation. The simplest method of preparation is a combination of the elements at a suitable temperature, usually in the range of 1100–2000°C. On a commercial scale, borides are prepared by the reduction of mixtures of metallic and boron oxides using aluminum, magnesium, carbon, boron, or boron carbide, followed by purification. Borides can also be synthesized by vapor-phase reaction or electrolysis.

To produce wear-resistant or hardened surfaces, thin layers of borides can be prepared on metal surfaces by reaction and diffusion (see METAL SURFACE TREATMENTS). Boride powders can be formed into monolithic shapes by cold pressing and sintering, or by hot pressing.

Uses. In spite of unique properties, there are few commercial applications for monolithic shapes of borides. They are used for resistance-heated boats (with boron nitride), for aluminum evaporation, and for sliding electrical contacts. There are a number of potential uses in the control and handling of molten metals and slags where corrosion and erosion resistance are important. Titanium diboride and zirconium diboride are potential cathodes for the aluminum Hall cells (see ALUMINUM AND ALUMINUM ALLOYS). Lanthanum hexaboride and cerium hexaboride are particularly useful as cathodes in electronic devices because of their high thermal emissivities, low work functions, and resistance to poisoning.

Boron Carbide

Boron and carbon form one compound, boron carbide *[12069-32-8]*, B_4C, although excess boron may dissolve in boron carbide, and a small amount of boron may dissolve in graphite (5). Usually excess carbon appears as graphite, except for the special case of boron diffused into diamonds at high pressures and temperatures, eg, 5 GPa (50 kbar) and 1500°C, where boron may occupy both interstitial and substitutional positions in the diamond lattice, a property utilized in synthetic diamonds (see CARBON, DIAMOND, SYNTHETIC).

Properties. Boron carbide has a rhombohedral structure consisting of an array of nearly regular icosahedra, each having twelve boron atoms at the vertices and three carbon atoms in a linear chain outside the icosahedra (3,4,6,7). Thus a descriptive chemical formula would be $B_{12}C_3$ *[12075-36-4]*. Each boron atom is bonded to five others in the icosahedron as well as either to a carbon atom or to a boron atom in an adjacent icosahedron. The structure is similar to that of rhombohedral boron (see BORON, ELEMENTAL). The theoretical density for $B_{12}C_3$ is 2.52 g mL. The rigid framework of relatively closely bonded atoms corresponds to a high melting point, about 2400°C, appreciable electrical conductivity, great hardness, about 27 GPa (270 kbar) on the Knoop scale (diamond indenters), and a high compressive strength. Brittleness limits its useful tensile strength to about 150 MPa (1.5 kbar) at 950°C; this, in combination with a moderate coefficient of thermal expansion, makes boron carbide sensitive to thermal shock. It is noticeably oxidized in air at 800–1000°C, and is a semiconductor having a room temperature resistivity of 0.001–0.1 Ω·m.

Boron carbide is resistant to most acids but is rapidly attacked by molten alkalies. It may be melted without decomposition in an atmosphere of carbon monoxide, but is slowly etched by hydrogen at 1200°C. It withstands metallic sodium fairly well at 500°C and steam at 300°C (8).

Preparation. Boron carbide is most commonly produced by the reduction of boric oxide with carbon in an electric furnace between 1400 and 2300°C. In the presence of carbon, magnesium reduces boric oxide to boron carbide at 1400–1800°C. The reaction is best carried out in a hydrogen atmosphere in a carbon tube furnace. By-product magnesium compounds are removed by acid treatment.

In general, the purified boron carbide is ultimately obtained as a granular solid that subsequently may be molded or bonded into useful shapes. To achieve high density and strength, it is hot pressed at 1800–2400°C in graphite molds.

Uses. Applications for boron carbide relate either to its hardness or its high neutron absorptivity (^{10}B isotope). Hot-pressed boron carbide finds use as wear parts, sandblast nozzles, seals, and ceramic armor plates; but in spite of its hardness, it finds little use as an abrasive. However, this property makes it particularly useful for dressing grinding wheels.

Boron carbide is used in the shielding and control of nuclear reactors (qv) because of its neutron absorptivity, chemical inertness, and radiation stability. For this application it may be molded, bonded, or the granular material may be packed by vibration.

Boron Nitride

Boron and nitrogen form one compound, boron nitride *[10043-11-5]*, BN, which may exist in a hexagonal, graphitelike form, hBN, having a layered structure and planar 6-membered rings of alternating boron and nitrogen atoms (3,9). On alternate sheets boron atoms are directly over nitrogen atoms. A rhombohedral form, rBN, is similar in density and structure, but the layers of sheets are stacked in groups of three instead of two as in hBN (10). A denser cubic form having a zinc-blende lattice (cBN) also exists in addition to an equally dense form having a wurtzite lattice (wBN). The latter two forms are, like diamond, thermodynamically stable only at high pressures but persist at normal pressures and temperatures because of the slowness of the transition.

Properties. Under nitrogen pressure hexagonal boron nitride melts at about 3000°C but sublimes at about 2500°C at atmospheric pressure. Despite the high melting point, the substance is mechanically weak because of the relatively easy sliding of the sheets of rings past one another (3). The theoretical density is 2.27 g mL and the resistivity is about 10^5 Ω·cm.

Hexagonal boron nitride is relatively stable in oxygen or chlorine up to 700°C, probably because of a protective surface layer of boric oxide. It is attacked by steam at 900°C, and rapidly by hot alkali or fused alkali carbonates. It is attacked slowly by many acids as well as alcohols (to form borate esters), acetone, and carbon tetrachloride. It is not wetted by most molten metals or many molten glasses.

The cubic and wurtzitic forms have similar chemical properties (11), but their reaction rates tend to be slower because of the denser structure. The dense forms expand to the graphite forms above ca 1700°C.

The cubic form resembles diamond in its crystal structure and is almost as hard. The theoretical density is 3.48 g mL. It is colorless and a good electrical insulator when pure; traces of impurities add color and make it semiconducting, eg, a few ppm of Be make it blue and *p*-type whereas small amounts of S, Si, or CN favor yellow, *n*-type crystals. It is possible to make *p–n* junctions by growing *n*-type material on *p*-type seed crystals (12). If this is done carefully in an alkaline-earth nitride bath using a temperature difference technique, as with large diamond crystals (see DIAMOND, SYNTHETIC), the resulting diodes are several mm in size and emit blue light when forward-biased (13,14).

Preparation. Hexagonal boron nitride can be prepared by heating boric oxide with ammonia, or by heating boric oxide, boric acid, or its salts with ammonium chloride, alkali cyanides, or calcium cyanamide at atmospheric pressure. Elemental nitrogen does not react with boric oxide even in the presence of carbon, though it does react with elemental boron at high temperatures. Boron nitride obtained from the reaction of boron trichloride or boron trifluoride with ammonia is easily purified.

Rhombohedral boron nitride can be prepared by heating a mixture of $NaBH_4$ and NH_4Cl rapidly to 750–1000°C (15). The presence of NaCl appears to favor the rhombohedral form.

The cubic zinc blende form of boron nitride is usually prepared from the hexagonal or rhombohedral form at high (4–6 GPa (40–60 kbar)) pressures and temperatures (1400–1700°C). The reaction is accelerated by lithium or alkaline-earth nitrides or amides, which are the best catalysts, and form intermediate liquid compounds with BN, which are molten under synthesis conditions (11,16). Many other substances can aid the transformation. At higher pressures (6–13 GPa) the cubic or wurtzitic forms are obtained without catalysts (17).

The wurtzite form differs only slightly from the cubic form, but it is not quite as stable. It is most easily obtained by static or dynamic compression of hBN or rBN at high pressures (17). In the presence of a liquid catalyst at high pressures, the wurtzite form changes rapidly to the cubic form. The change occurs more slowly without a catalyst above 6 GPa (60 kbar) (18).

Many attempts have been made to synthesize cubic BN at low pressures by some sort of chemical vapor deposition process in analogy with the low pressure deposition of diamond from methane in the presence of H atoms (see DIAMOND, SYNTHETIC). However, the amounts of cubic BN produced in this fashion in 1991 were miniscule, and were at best thin layers only a few dozen atoms thick (12).

Uses. Hot-pressed hBN is useful for high temperature electric or thermal insulation, vessels, etc, especially in inert or reducing atmospheres, and for special materials such as III-V semiconductors (qv). Its low thermal expansion makes it resistant to thermal shock. The powder can be used as a mold release agent or as thermal insulation. Boron nitride is also available in fiber form (19). BN deposited pyrolytically on refractory substrates at 1200–1800°C has a turbostratic structure and low porosity; it has greater chemical resistance and is impervious to helium.

The greatest use of cubic boron nitride is as an abrasive under the name Borazon, in the form of small crystals, 1–500 μm in size. Usually these crystals are incorporated in abrasive wheels and used to grind hard ferrous and nickel-based alloys, ranging from high speed steel tools and chilled cast-iron to gas turbine parts. The extreme hardness of the crystals and their resistance to attack by air and hot metal make the wheels very durable, and close tolerances can be maintained on the workpieces.

The cubic BN crystals may also be bonded into strong bodies that make excellent cutting tools for hard iron and nickel-based alloys. Such tools produce red-hot chips and permit the wider use of tough, high temperature alloys which would otherwise be prohibitively difficult to shape (12,20,21) (see ABRASIVES).

Economic Aspects

In 1990 the sales value of most borides was less than a million dollars per year, with the most important being the rare-earth hexaborides, used for electronic cathodes. The sales value of boron carbide is also small compared with other hard materials and abrasives. The sales of the soft forms of boron nitride, at prices in the range $15–100 kg, run to a few million dollars per year in the United States. The Norton Co. and Carborundum Co. are significant producers of hBN and boron carbide. The sales of the cubic form of boron nitride amount to over several dozen million dollars per year, worldwide, on account of its great popularity as an industrial abrasive in many industries and its high value ($15,000 kg). A large machine-tool industry based on this abrasive has sprung up. The General Electric Co. is the principal producer in the United States, but production in Japan and Russia is comparable.

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BORON HALIDES

The boron trihalides boron trifluoride *[7637-07-2]*, BF_3, boron trichloride *[10294-34-5]*, BCl_3, and boron tribromide *[10294-33-4]*, BBr_3, are important industrial chemicals having increased usage as Lewis acid catalysts and in chemical vapor deposition (CVD) processes (see ELECTRONIC MATERIALS). Boron halides are widely used in the laboratory as catalysts and reagents in numerous types of organic reactions and as starting material for many organoboron and inorganic boron compounds. An exhaustive review of the literature on boron halides up to 1984 is available (1–5). Of particular interest are review articles on BCl_3 (1), BBr_3 (2), and boron triiodide *[13517-10-7]*, BI_3 (3). An excellent review on diboron tetrahalides and polyhedral boron halides is available (6), as is a discussion of the economic aspects of the commercially important boron halides (7). For a discussion of BF_3, see FLUORINE COMPOUNDS, INORGANIC, BORON TRIFLUORIDE.

BORON TRIHALIDES

Properties

Boron trihalides, BX_3, are trigonal planar molecules which are sp^2 hybridized. The X–B–X angles are 120°. Important physical and thermochemical data are presented in Table 1 (8–14). Additional thermodynamic and spectroscopic data may be found in the literature (1–5).

Table 1. Physical Properties of the Boron Trihalides

Property	BCl_3	BBr_3	BI_3	References BCl_3	BBr_3	BI_3
mp, °C	107	46	49.9	8	8	8
bp, °C	12.5	91.3	210	8	8	8
density[a], g mL (liq)	1.434_4^0 1.349_4^{11}	2.643_4^{18}	3.35	9	10	
critical temperature, °C	178.8	300		8	8	
critical pressure, kPa[b]	3901.0			11		
vapor pressure, kPa[b]				11	10	12
80°C	0.53	[c]				
40°C	8.9					
0°C	63.5					
40°C	243					
80°C	689					
viscosity, mPa·s (cP)	[d]	[d]		9	10	
ΔH_f^0, kJ mol, gas[e]	403	206	−18	13	13	13
ΔH_{vap}, kJ mol[e]	23.8	34.3		13	13	
C_p, J(mol·°C), for gas at 25°C[e]	62.8	67.78		11	11	
C_p, J (mol·°C), for liquid at 25°C[e]	121	128		11	11	
ΔH_{hydrol}, kJ mol, liquid at 25°C[e]	289	351		11	11	
ΔH_{fus}, J g at mp[e]	18			11		
B–X bond energy, kJ mol[e]	443.9	368.2	266.5	14	14	14
B–X distance, nm	0.173	0.187	0.210	14	14	14

[a] For BCl_3: ρ 1.3730−2.159 × 10 ^{3}°C − 8.377 × 10 ^{7}°C ; from 44 to 5°C. Superscript indicates temperature of measurement. For BBr_3: ρ 2.698−2.996 × 10^{-3}°C; from 20 to 90°C.

[b] To convert kPa to mm Hg, multiply by 7.50.

[c] For BBr_3: log(pressure) = [6.9792 1311 (°C + 230)] 0.8752 ; from 0–90°C.

[d] For BCl_3: η 0.34417 (1 6.9662 × 10 ^{3}°C 5.9013 × 10 ^{6}°C) ; from 40 to 10°C. For BBr_3: log η (333 K) 1.257; from 0–90°C.

[e] To convert J to cal, divide by 4.184.

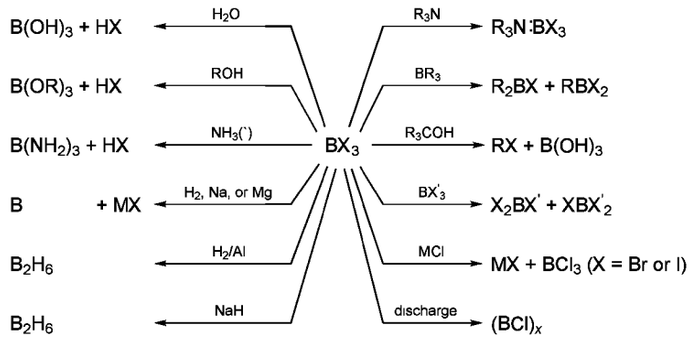
The boron trihalides are strong Lewis acids, however, the order of relative acid strengths, $BI_3 > BBr_3 > BCl_3 > BF_3$, is contrary to that expected based on the electronegativities and atomic sizes of the halogen atoms. This anomaly has been explained in terms of boron–halogen π-bonding, which increases from BI_3 to BF_3 (15,16). The Lewis acidity of the boron trihalides strongly influences their chemistry (17–20). The trihalides react with Lewis bases containing O, S, N, P, or As atoms to form donor–acceptor complexes. For donor compounds containing active hydrogen, such as NH_3, PH_3, AsH_3, primary and secondary amines, and lower alcohols, BCl_3, BBr_3, and BI_3 react to liberate the corresponding hydrogen halide. Tertiary alcohols and the boron trihalides yield the alkyl halide and boric acid. The boron trihalides hydrolyze readily in water or moist air to produce boric acid and hydrogen halides.

BCl_3, BBr_3, and BI_3 undergo exchange reactions to yield mixed boron halides. Exchange reactions also occur with trialkyl, triaryl, trialkoxy, or triaryloxy boranes and with diborane. Anhydrous metal bromides and iodides can be prepared by the exchange reaction of the metal chloride or oxide and BBr_3 or BI_3 (21).

Boron trihalides can be reduced to elemental boron by heating and presence of alkali metals, alkaline-earth metals, or H_2 (22–26); such reductions

can also yield boron subhalides, eg, chloroborane *[20583-55-5]*, BCl, B_xCl_x, dichloroborane *[10325-29-0]*, $HBCl_2$, (27–30), and or diborane *[19287-45-7]*, B_2H (27–30). Metal hydrides also react with BX_3 to yield diborane (31–33).

Some of the general reactions for the boron trihalides where X represents Cl, Br, or I and X′ a different halogen, are



Reactions of boron trihalides that are of commercial importance are those of BCl_3, and to a lesser extent BBr_3, with gases in chemical vapor deposition (CVD). CVD of boron by reduction, of boron nitride using NH_3, and of boron carbide using CH_4 on transition metals and alloys are all technically important processes (34–38). The CVD process is normally supported by heating or by plasma formed by an arc or discharge (39,40).

Manufacturing and Processing

Boron Trichloride. Boron trichloride is prepared on a large scale by the reaction of Cl_2 and a heated mixture of borax *[1303-96-4]*, $Na_2BO_4O_7 \cdot 10H_2O$, and crude oil residue (41) in a rotary kiln heated to 1038°C. Borax is fed at the rate of 1360 kg h and sprayed with 635 kg h of 17% residue crude oil. The heated mixture then reacts with Cl_2 at 760°C in a separate reactor to yield BCl_3. On a smaller scale, BCl_3 can be prepared by the reaction of Cl_2 and a mixture of boron oxide *[1303-86-2]*, B_2O_3, petroleum coke, and lampblack in a fluidized bed (42). Other methods for the preparation of BCl_3 from oxygen-containing boron compounds are also known (1,43–46).

A convenient laboratory method for the preparation of BCl_3 is by the reaction of $AlCl_3$ and BF_3 or BF_4 (47–49). More recently a patent describing the preparation of BCl_3 by halogenating $B(OH)_3$ or esters of $B(OH)_3$ using an excess of the oxychloride of S or P in the presence of a dessicant and catalytic amounts of Fe, Co, or Ni, at temperatures below 100°C was issued (50). This process eliminates formation of carbonic dichloride *[75-44-5]*, $COCl_2$, a common impurity in large-scale production of BCl_3. Other common impurities associated with the preparation of BCl_3 are CO, CO_2, Cl_2, HCl, $FeCl_3$, $SiCl_4$, $AsCl_3$, and SO_2. Methods for purification include distillation (51–53), sometimes in the presence of KCl; activated charcoal or polyphenylene dioxide (54); adsorption desorption on silica gel (55,56); countercurrent crystallization (53); and passage of impure gas through Ti sponge (57), molten Zn (58), Cu or charcoal at elevated temperatures (59). $COCl_2$ can also be destroyed by pyrolysis (60), by a discharge, or irradiation using a radio frequency or an electron beam (61,62), or by uv photolysis using a laser (60,63,64).

Boron Tribromide. Boron tribromide is produced on a large scale by the reaction of Br_2 and granulated B_4C at 850–1000°C (65) or by the reaction of HBr with CaB at high temperatures (66). Reaction of Br_2 and a mixture of B_4C and CaB at 900–1200°C is used to prepare high purity BBr_3 (67). Another method for preparing high purity BBr_3 is the reaction of the two elements, B and Br_2, at 750°C in N_2 atmosphere, followed by fractional distillation (68).

Most of the methods for preparing BBr_3 are similar to those for preparation of BCl_3. A convenient laboratory preparation involves reaction of $AlBr_3$ and BF_3 or BF_4 (2). A procedure for the preparation of labeled $^{10}BBr_3$ from the reaction of $^{10}BF_4$ and $AlBr_3$ has also been described (69).

Boron Triiodide. Boron triiodide is not manufactured on a large scale. Small-scale production of BI_3 from boron and iodine is possible in the temperature range 700–900°C (70–72). Excess I_2 can be removed as SnI_4 by reaction with Sn, followed by distillation (71). The reaction of metal tetrahydroborates and I_2 is convenient for laboratory preparation of BI_3 (73,74). BI_3 can also by synthesized from B_2H and HI in a furnace at 250°C (75), or by the reaction of B with excess AgI or CuI between 450–700°C, under vacuum (76). High purity BI_3 has been prepared by the reaction of I_2 with mixtures of boron carbide and calcium carbide at elevated temperatures.

In addition to distillation (73), BI_3 can be purified by sublimation under reduced pressure (77).

Production, Shipment, and Economic Aspects

The 1989 production of BCl_3 was estimated at 225–250 metric ton and that of BBr_3 at 23 metric ton (7). The 1989 figures are roughly double those of 1976 (78), showing substantial growth. Consumption during 1989 was estimated at 190–215 metric ton for BCl_3 and 18 t for BBr_3 (7). Kerr-McGee Corporation (Henderson, Nevada) is the largest producer of BCl_3 in the United States, having an annual capacity of 365 metric ton (7); it also produces BBr_3 having an annual capacity of 11 t. Olin Corp. (Seward, Illinois) is the next largest producer, having annual capacities of 9 t for BCl_3, and 15 t for BBr_3 (7). Texas Instrument produces technical-grade (99.3%) BBr_3 (7). Kerr-McGee Corp.'s Nov. 1991 prices were $16.76 kg of 99.9% BCl_3 and $81.57 kg of 99.9% BBr_3. Prices for technical-grade BCl_3 were $8.38 kg in 816 kg steel cylinders. Substantial quantities of BCl_3 are exported, mainly to Japan (7). BCl_3 is shipped in steel cylinders (0.9-, 45-, 590-, and 817-kg, net); BBr_3 is shipped in glass bottles (0.45- and 2.3-kg, net) and 91-kg (net) monel drums (11). Both BCl_3 and BBr_3 are classed as corrosive liquids, and must be shipped by private carriers.

Analytical and Test Methods, Specification, and Safety Factors

Analysis for boron, halide, free halogen, and silicon is carried out by standard methods following hydrolysis of BX_3 (11,79). Specifications for BCl_3 and BBr_3 supplied by Kerr-McGee Corp. are given in Table 2.

Table 2. Specifications for BCl_3 and BBr_3[a]

	BCl_3, wt %		BBr_3, wt %	
Assay	Specification	Typical	Specification	Typical
BX_3	99.9 min	99.95	99.9 min	99.98

Br_2		0.05 max	0.01
Cl_2	0.01 max		
$COCl_2$	0.09 max		
Si	0.001 max		0.0002[b]

[a] Ref. 78.

[b] Other impurities in wt % are typically P, 0.002; Fe, 0.003; and Mg, 0.0002.

Boron trichlorides are highly reactive, toxic, and corrosive; these trihalides (BCl_3, BBr_3, BI_3) react vigorously, even explosively, with water. High temperature decomposition of BX_3 can yield toxic halogen-containing fumes. Safe handling, especially of BCl_3, has been reviewed (11,80).

Uses

Boron Trichloride. Approximately 75–95% of the BCl_3 consumed in the United States is used to prepare boron filaments by CVD (7). These high performance fibers are used to reinforce composite materials (qv) made from epoxy resins and metals (Al, Ti). The principal markets for such composites are aerospace industries and sports equipment manufacturers.

Another important use of BCl_3 is as a Friedel-Crafts catalyst in various polymerization, alkylation, and acylation reactions, and in other organic syntheses (see FRIEDEL-CRAFTS REACTION). Examples include conversion of cyclophosphazenes to polymers (81,82); polymerization of olefins such as ethylene (75,83–88); graft polymerization of vinyl chloride and isobutylene (89); stereospecific polymerization of propylene (90); copolymerization of isobutylene and styrene (91,92), and other unsaturated aromatics with maleic anhydride (93); polymerization of norbornene (94), butadiene (95); preparation of electrically conducting epoxy resins (96), and polymers containing B and N (97); and selective demethylation of methoxy groups ortho to OH groups (98).

BCl_3 is also used for the production of halosilanes, in the preparation of many boron compounds (1,4,5), in the production of optical wave guides (99), and for the prevention of solid polymer formation in liquid SO_3 (11); for the removal of SiO_2 from SiC powders (100), carbochlorination of kaolinitic ores (101), and removal of impurities from molten Mg (99). It is also used as a critical solvent in metal recovery from chlorination processes (102), for the removal of potential catalyst poisons from hydrocarbon oils (103), and in the production of lithium–thionyl chloride batteries (104). BCl_3 is used by Eagle Pitcher Industries to manufacture isotopically enriched crystalline boron (7). Other than production of boron fibers, important CVD processes involving BCl_3 include: production of boron carbide-coated carbon fiber (105,106); doping Si or Ge with B and for doping electric or photoconducting polymers, in the preparation of scratch-resistant silicon-based coatings, and in glass-fiber technology (5); production of boron nitride (5,107–109), and metal borides (5). BCl_3 is also used in reactive ion etching and plasma etching in the production of silicon-integrated circuits and devices, in the dry etching of boron nitride, gallium arsenide, and SnO_2 (5), and Al–Si (110,111).

Boron Bromide. Approximately 30% of BBr_3 produced in the United States is consumed in the manufacture of proprietory pharmaceuticals (qv) (7). BBr_3 is used in the manufacture of isotopically enriched crystalline boron, as a Friedel-Crafts catalyst in various polymerization, alkylation, and acylation reactions, and in semiconductor doping and etching. Examples of use of BBr_3 as a catalyst include copolymerization of butadiene with olefins (112); polymerization of ethylene and propylene (113), and *N*-vinylcarbazole (114); in hydroboration reactions and in tritium labeling of steroids and aryl rings (5).

BBr_3 is a very useful reagent for cleaving ethers, esters, lactones, acetals, and glycosidic bonds; it is used to deoxygenate sulfoxides and in the preparation of image-providing materials for photography (5).

Boron Triiodide. There are no large-scale commercial uses of boron triiodide. It can cleave ethers without affecting aldehyde groups and thus finds use in the synthesis of the antibiotic frustulosin (115,116). BI_3 is used to prepare SnI_4, SbI_3, and TiI_4 (117) in 99–100% yield. It is used to clean equipment for handling UF (118) and in the manufacture of lithium batteries (119).

BORON SUBHALIDES

Boron subhalides are binary compounds of boron and the halogens, where the atomic ratio of halogen to boron is less than 3. The boron monohalides, BCl, *[20583-55-5]*, bromoborane(1) *[19961-29-6]*, BBr, and iodoborane(1) *[13842-56-3]*, BI, are unstable species that have been observed spectroscopically when the respective trihalides were subjected to a discharge (5). Boron dihalide radicals have been studied, and structural and thermochemical data for these species ($\cdot BX_2$) have been deduced (5).

Diboron tetraflouride *[13965-73-6]*, B_2F_4, diboron tetrachloride *[13701-67-2]*, B_2Cl_4, diboron tetrabromide *[14355-29-4]*, B_2Br_4, and diborontetraiodide *[13703-80-5]*, B_2I_4, are well known, but thermally unstable compounds. Diboration of unsaturated organic molecules using B_2X_4 species is of considerable interest because of the similarity to the very well known hydroboration reaction. In spite of the interesting chemistry of the diboron tetrahalides and also the polyhedral boron halides (6), these compounds have not yet found commercial applications.

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BORON HYDRIDES, HETEROBORANES, AND THEIR METALLA DERIVATIVES

The boron hydrides, including the polyhedral boranes, heteroboranes, and their metalla derivatives, encompass an amazingly diverse area of chemistry. This class contains the most extensive array of structurally characterized cluster compounds known. Included here are many novel clusters possessing idealized molecular geometries ranging over every point group symmetry from identity (C_1) to icosahedral (I_h). Because boron hydride clusters may be considered in some respects to be progenitorial models of metal clusters, their development has provided a framework for the development of cluster chemistry in general as well as for chemical bonding theory.

The first definitive studies of boron hydrides were carried out by Alfred Stock in Germany starting about 1912 (1). Through extensive and now classic synthetic studies, the field of boron hydride chemistry was founded with the isolation of a series of highly reactive, air-sensitive, and volatile compounds of general composition B_nH_{n+4} and B_nH_{n+} . This accomplishment required the development of basic vacuum line techniques for the manipulation of air-sensitive compounds (see VACUUM TECHNOLOGY). An American effort in boron hydride research was subsequently initiated by H. I. Schlesinger. His student, H. C. Brown, eventually developed the hydroboration procedures which are now so important to organic chemistry and for which, in 1979, he received a Nobel Prize (2).

Following World War II, activity in boron hydride research increased tremendously as a result of classified government research programs on high energy fuels such as the HERMES project (3). In the 1950s, research on boron hydride energetic materials continued. Research was initially directed toward the development of new fuels for aircraft, such as the B-70 Valkyrie long-range bomber, and eventually led to research on solid rocket propellants (see EXPLOSIVES AND PROPELLANTS). Similar research was also being conducted during this period in Russia. When the U.S. programs were declassified in 1964, many of the important findings, including the discovery of carboranes, were published. Although much information from these enormous governmental efforts has never been published, boron hydride materials have since resulted from government stockpiles produced prior to 1964.

The structural and theoretical aspects of boron hydrides were delineated through x-ray diffraction, theoretical analyses of bonding, and structure and reactivity studies. W. N. Lipscomb received the 1976 Nobel Prize for his definitive work in this area of boron hydride chemistry (4). The emergence of a theoretical understanding of boron hydrides and the residual momentum of the high energy fuels program led to a rapid proliferation of significant new boron hydride compounds and the elaboration of their chemistry. A half-century after the first report of highly reactive boron hydrides, the most stable classes of boron hydrides, the polyhedral borane anions, carboranes, and metallacarboranes were discovered. The isomeric icosahedral carborane $C_2B_{10}H_{12}$ was reported almost simultaneously by American industrial chemists and by workers in Russia (5). The highly fruitful marriage of transition metal and carborane cluster chemistry leading to the metallacarboranes soon followed (6).

Nomenclature

The nomenclature of boron hydride derivatives has been somewhat confusing and many inconsistencies exist in the literature. The structures of some reported boron hydride clusters are so complicated that only a structural drawing or graph, often accompanied by explanatory text, is used to describe them. Traditional nomenclature systems often can be used to describe compounds unambiguously, but the resulting descriptions may be so long and unwieldy that they are of little use. The IUPAC (7) and the Chemical Abstract Service (8) have made recommendations, and nomenclature methods have now been developed that can adequately handle nearly all clusters compounds; however, these methods have yet to be widely adopted. For the most part, nomenclature used in the original literature is retained herein.

The neutral boron hydrides are termed boranes. The molecule BH_3 is called borane or borane(3) *[13283-31-3]*. For more complex polyboranes, the number of boron atoms is indicated by the common prefixes di-, tri-, tetra-, etc, and the number of hydrogens (substituents) is given by an arabic numeral in parentheses following the name. For example, B_5H_{11} is named pentaborane(11) *[18433-84-6]*, $B_{20}H_1$ is named icosaborane(16) *[12008-84-3]*, and $B_{10}H_{12}I_2$ is diiododecaborane(14) *[23835-60-1]*. The position of the substituents can be designated precisely from framework numbering conventions. The numbering conventions for selected polyhedra are given in Figure 1. Because other numbering systems are often also used, it is advisable to refer to structural diagrams.

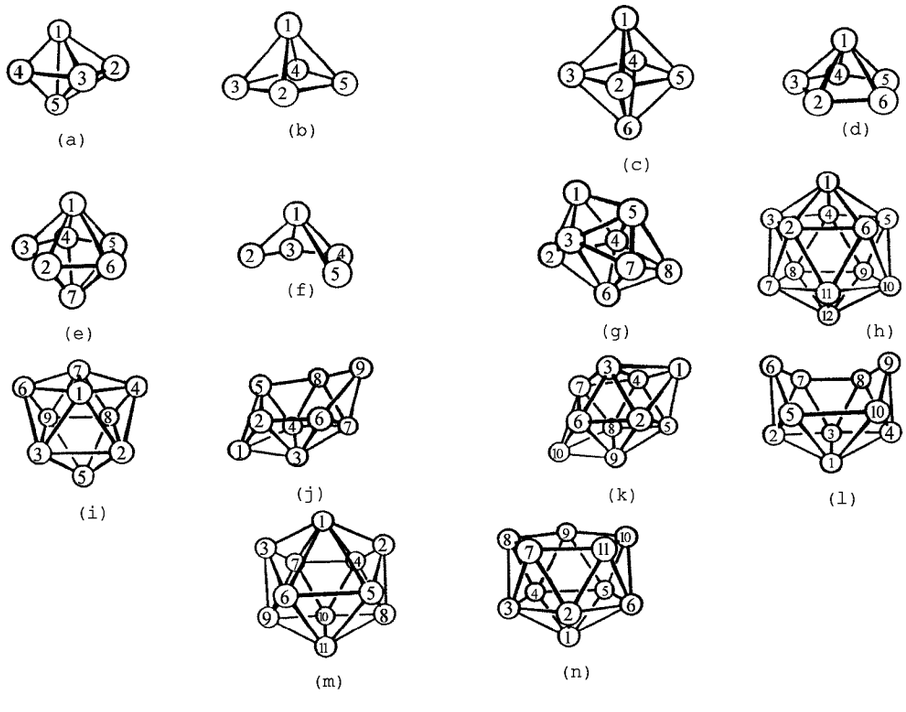


Fig. 1. Numbering conventions for selected borane polyhedra (7) discussed in text.

Borane polyhedra have both closed and open skeletons and it has become common practice to include the appropriate structural classification in the compound's name. Closed polyhedra having only triangular faces are termed *closo*, and open structures are designated *nido, arachno*, or *hypho*. For instance, more complete names for the previous examples are *arachno*-pentaborane(11), *closo*-icosaborane(16), and 2,4-diiodo-*nido*-decaborane(14). Boron hydride anions are generally termed hydroborates using prefixes to designate the number of hydrogens and borons; the charge follows the name in parentheses. For example, $Na[BH_4]$ is sodium tetrahydroborate(1-) *[16940-66-2]*, $K_2[B_{10}H_{10}]$ is potassium decahydro-*closo*-decaborate(2-) *[12447-89-1]*, and the 2,4-dichlorododecahydro-*nido*-decaborate(2-) anion *[51668-03-2]* is $[2,4\text{-}Cl_2B_{10}H_{12}]^{2-}$.

When a boron atom of a borane is replaced by a heteroelement, the compounds are called carbaboranes, phosphaboranes, thiaboranes, azaboranes, etc, by an adaptation of organic replacement nomenclature. The numbering of the skeleton in heteroboranes is such that the heteroelement is given the lowest possible number consistent with the conventions of the parent borane. Thus $C_2B_3H_5$ is dicarba-*closo*-pentaborane(5) and could occur as the 1,2-, 2,3-, or 1,5-isomeric forms (1,2-dicarba-*closo*-pentaborane(5) *[23777-70-0]*, 2,3-dicarba-*closo*-pentaborane(5) *[30396-61-3]*, and 1,5-dicarba-*closo*-pentaborane(5) *[20693-66-7]*) (see Fig. 1**a**). When different heteroelements occur in combination in a polyhedron, *Chemical Abstracts* gives priority by descending group number and increasing atomic number within a group, eg, $1,2\text{-}PCB_{10}H_{11}$ is 1-phospha-2-carba-*closo*-decaborane(11) *[30112-97-1]*; however, the hierarchy in the original literature often gives the lowest number to the element of lowest atomic number, eg, $1,2\text{-}CPB_{10}H_{11}$ or 1-carba-2-phospha-*closo*-dodecaborane(11) *[30112-97-1]*. This convention carries over to the metallaboranes and metallaheteroboranes when a metal occupies a polyhedral vertex. Examples are 9,9-bis(triphenylphosphine)-6-thia-9-platina-*nido*-decaborane(10) *[52628-81-6]*, $9,9\text{-}[P(C_6H_5)_3]_2\text{-}6,9\text{-}SPtB_8H_{10}$, 3-$\eta^5$-cyclopentadienyl-2-dimethyl-1,2-dicarba-3-ferra-*closo*-dodecaborane(11) *[66750-82-1]*, $3\text{-}(\eta^5\text{-}C_5H_5)\text{-}1,2\text{-}(CH_3)_2\text{-}3,1,2\text{-}FeC_2B_9H_9$. The arabic numeral in parentheses following the name does not include exopolyhedral ligands bonded to the metal, only the total of the hydrogen atoms plus other substituents bonded to boron and main group heteroelements. Examples of metallaborane anions are the 1-η^5-cyclopentadienyl-1-nickela-undecahydro-*closo*-undecaborate(1-) ion, $[(\eta^5\text{-}C_5H_5)Ni(B_{11}H_{11})]^-$, and the 2-$\eta^5$-cyclopentadienyl-2-cobalta-heptahydro-*nido*-tetraborate(1-) ion, $[2\text{-}(\eta^5\text{-}C_5H_5)\text{-}2\text{-}CoB_4H_7]^-$.

A variety of heteroboranes, metallaboranes, and metallaheteroboranes exist that contain more than one interconnected polyhedral cluster. These complex clusters are referred to as conjuncto-boranes. Conjuncto-boranes may be interconnected by sharing a single common boron atom, having a direct B–B bond between two clusters, sharing two boron atoms at a polyhedral edge or three boron atoms at a face, or more extensive polyhedral fusion by the sharing of four or more boron atoms between clusters. Examples include the *commo*-7,7′-bis(dodecahydro-7-nickela-*nido*-undecaborate)(2-) dianion *[31388-28-0]*, $[7,7'\text{-}Ni(B_{10}H_{12})_2]^{2-}$, and the decahydro-2,11-bis(η^5-cyclopentadienyl)-2,11-dicobalt-1-carba-*closo*-dodecaborate(1-) ion *[59422-34-3]*, $[2,11\text{-}(\eta^5\text{-}C_5H_5)_2\text{-}2,11,1\text{-}Co_2CB_9H_{10}]^-$. The *commo* prefix is often used to indicate that the metal vertex is shared by two polyhedra. The *commo* nomenclature of metallaboranes and metallaheteroboranes is a widely used special case of the IUPAC recommended conjuncto nomenclature.

Structural Systematics

Because the polyhedral boron hydrides are cage molecules, which usually possess triangular faces, their idealized geometries can be described accurately as deltahedra or deltahedral fragments. The left-hand column of Figure 2 illustrates the deltahedra containing $n = 6-12$ vertices: the octahedron, pentagonal bipyramid, bisdisphenoid, symmetrically tricapped trigonal prism, bicapped square antiprism, octadecahedron, and icosahedron. These idealized structures are convex deltahedra except for the octahedron, which is not a regular polyhedron. The left-hand column of Figure 2 also represents the class of deltahedral *closo* molecules from which the other idealized structures (deltahedral fragments) can be generated systematically. Any *nido* or *arachno* cluster can be generated from the appropriate deltahedron by ascending a diagonal from left to right. This progression generates the *nido* structure (center column) by removing the most highly connected vertex of the deltahedron, and the *arachno* structure (right column) by removal of the most highly connected atom of the open (nontriangular) face of the *nido* cluster. The structural correlations shown in Figure 2 were formulated in 1971 (9), and subsequently elaborated (10,11). The terms *closo, nido, arachno*, and *hypho* are derived from Greek and Latin and imply closed, nestlike, weblike, and netlike structures, respectively. These classifications apply equally well to boranes, heteroboranes, and their metalla analogues, and are intimately connected to a quantity known as the framework, or skeletal, electron count. The partitioning of electrons into framework and exopolyhedral classes allows for predictions of structures in most cases, even though these systematics are not concerned explicitly with the assignments of localized bonds within the polyhedral skeletons of these molecules. That is, the lines depicting the skeletons of the structures illustrated are not electron-pair, or "electron precise", bonds. The lines merely serve to join nearest neighbors and illustrate cluster geometries. However, exopolyhedral lines do represent the usual electron precise bonds.

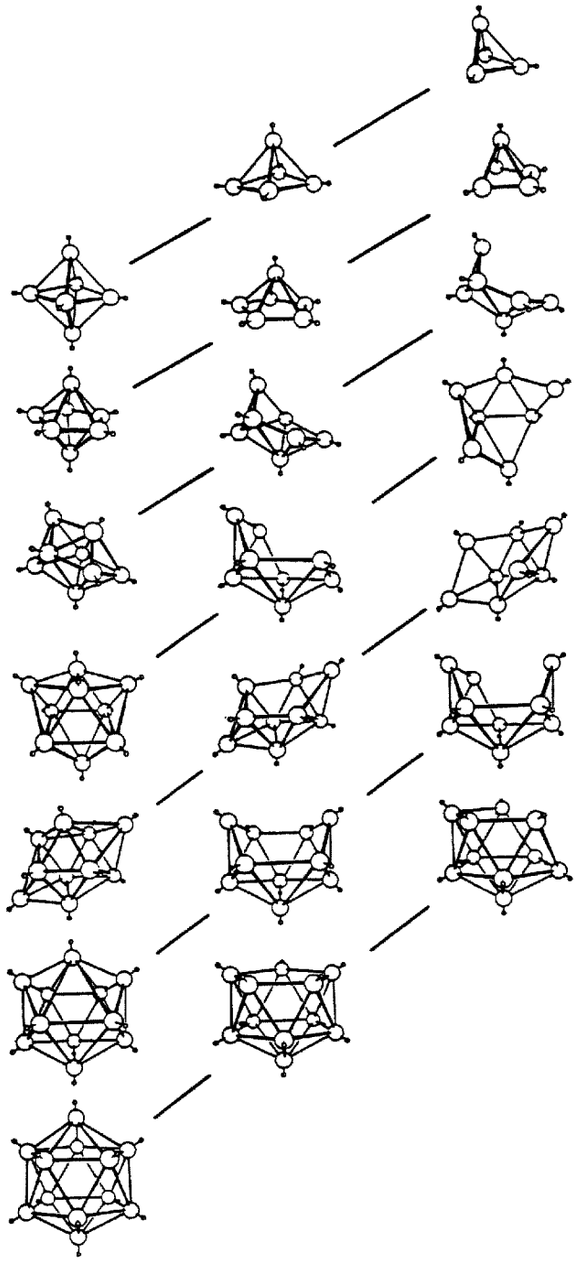


Fig. 2. Idealized deltahedra and deltahedral fragments for *closo, nido*, and *arachno* boranes and heteroboranes. From left to right the vertical columns give generic *closo, nido*, and *arachno* frameworks; bridge hydrogens and BH_2 groups are not shown, but when appropriate they are placed around the open (nontriangular) face of the framework (see text).

Proposal of a structure from Figure 2 for a given borane or heteroborane proceeds by: (*1*) selecting the row that corresponds to the number of framework atoms, or polyhedral vertices, *n*; and (*2*) determining the number of electrons that can reasonably be assigned to bonding within the polyhedral skeleton as opposed to exopolyhedral bonds. Framework electron counts of $2n + 2$, $2n + 4$, $2n + 6$, and $2n + 8$ correspond to the cluster classifications *closo, nido, arachno*, and *hypho*, respectively. For *closo, nido*, and *arachno* electron counts, a structure in the appropriate column of Figure 2 is suggested. These systematics emphasize the oxidation–reduction relationship of *closo–nido–arachno–hypho* interconversions for clusters having the same number of vertices. Boranes of the *hypho* class are relatively rare and are not included in Figure 2. The term *klado* is recommended by the IUPAC to designate the equally rare class of compounds having a $2n + 10$ framework electron count. The term *capo* has been proposed to describe boranes, such as $B_{10}H_{10}$, having a $2n$ framework electron count. Other empirical rules refer to the preferred placement of heteroatoms and so-called extra hydrogen atoms in these clusters. The correlation of skeletal electron count with structure is generally applicable to the metallaborane derivatives as well as to other types of cluster molecules such as carbocations (12) and metal clusters (11,13,14).

It should be noted that the eight-vertex *nido* cage shown in Figure 2 is more open than would be expected for a cluster resulting from the simple removal of one vertex from the nine-vertex *closo* cage. However, this is the observed geometry for known eight-vertex boranes and carboranes. This apparent anomaly reflects a pattern that exists for *nido* cages containing only boron and or carbon framework atoms in which, once cages become large enough, there is an alternation of five- and six-membered open faces (15). That is, 6-, 8-, 10-, and 12-vertex *nido* boranes and carboranes have six-membered open faces and 7-, 9-, and 11-vertex boranes and carboranes have five-membered open faces. Arguments can be made that rationalize this observed pattern in terms of charge density of atoms at the open face.

Closo Clusters ($2n + 2$ Systems). The assignment of valence electrons and the factoring out of those electrons involved in exopolyhedral bonds provides $2n$ framework electrons for a B_nH_n molecule, two electrons short of the $2n + 2$ *closo* count. In fact, stable neutral B_nH_n molecules are not known; however, the $[B_nH_n]^{2-}$ anions (n 6–12) and the neutral isoelectronic $C_2B_{n-2}H_n$ carboranes (n5–12) are very stable. These are the best known examples of *closo* molecules. Thus, in these respective cases, the double negative charge and the two C–H groups that donate one more valence electron each than a B–H group, furnish the two electrons required to achieve the $2n + 2$ framework electron count. In general, substitution of other moieties for a B–H vertex alters the number of framework electrons contributed by a particular vertex, but as long as the total remains $2n + 2$, the molecule is classified as *closo*. The number of electrons contributed to the framework electron count by a specific vertex group has been generalized in the form of an equation (14).

For main group elements the number of framework electrons contributed is equal to ($v + x - 2$) where v is the number of valence shell electrons of that element, and x is the number of electrons from ligands, eg, for H, $x = 1$, and for Lewis bases, $x = 2$. Examples of $2n + 2$ electron count boranes and heteroboranes, and the number of framework electrons contributed by their skeletal atoms, are given in Table 1.

Table 1. Electron Counting for 2n + 2, 2n + 4, and 2n + 6 Systems[a]

Compound	Framework electron contribution						
	Boron[b]	Carbon[b]	Heteroatom[b]	Extra hydrogens	Charge	Total	Ref.
			Closo $(2n + 2)e^-$ *systems*				
$C_2B_3H_5$	3(2)	2(3)			0	12	16
$[B_6H_6]^{2-}$	6(2)				2	14	17
$(CH_3)GaC_2B_4H$[c]	4(2)	2(3)	1(2)		0	16	18
$[B_8H_8]^{2-}$	8(2)				2	18	16
$C_2B_7H_9$	7(2)	2(3)			0	20	19
$[CB_9H_9^-]$	9(2)	1(3)			1	22	20
$C_2B_9H_{11}$	9(2)	2(3)			0	24	21
$SB_{11}H_{11}$	11(2)		1(4)		0	26	22
$SnC_2B_9H_{11}$	9(2)	2(3)	1(2)		0	26	23
$CPB_{10}H_{11}$	10(2)	1(3)	1(3)		0	26	24
			Nido $(2n + 4)e^-$ *systems*				
$C_2B_3H_7$	3(2)	2(3)		2	0	14	25
$C_3B_3H_7$	3(2)	3(3)		1	0	16	26
C_4B_2H	2(2)	4(3)			0	16	27
SB_8H_{10}	8(2)		1(4)	2	0	22	22
SB_9H_{11}	9(2)		1(4)	2	0	24	22
$[CPB_9H_{10}]^{2-}$	9(2)	1(3)	1(3)		2	26	24
			Arachno $(2n + 6)e^-$ *systems*				
B_5H_{11}	5(2)			6	0	16	28
$C_2B_7H_{13}$	7(2)	2(3)		4	0	24	29
$[SB_9H_{13}^-]$	9(2)		1(4)	3	1	26	22

[a] Where n is the number of non-hydrogen atoms in the cage structure.

[b] Number of atoms multiplied by, in parentheses, the number of electrons contributed to the framework gives the total electron contribution for the element.

[c] The CH_3 groups are outside the cage.

Nido Clusters ($2n + 4$ Systems). Many *closo* boranes and heteroboranes add two electrons and undergo a concomitant structural transformation from a deltahedron to a deltahedral fragment. For instance, *closo*-2,6-$C_2B_9H_{11}$ *[17764-89-0]*, ($2n + 2 = 24e^-$), is readily reduced to [*nido*-7,9-$C_2B_9H_{11}]^{2-}$; *[39469-99-3]*, ($2n + 4 = 26e^-$), and conversely [*nido*-7,9-$C_2B_9H_{11}]^{2-}$; may be oxidized to the *closo* cage (30). An effective reduction also occurs upon addition of donors to these molecules, eg, the molecules *closo*-$C_2B_4H_6$ and *closo*-$C_2B_9H_{11}$ open upon addition of amines to give *nido*-$C_2B_4H_6 \cdot NR_3$ (31) and *nido*-$C_2B_2H_{11} \cdot NR_3$ (32). Such additions of donor groups can formally be regarded as equivalent to additions of H^- ;, ie, *nido*-$C_2B_4H_6 \cdot L$ and *nido*-$C_2B_9H_{11} \cdot L$ are analogous to $[C_2B_4H_7]^-$; and $[C_2B_9H_{12}]^-$;, respectively. Other examples of *nido* molecules are given in Table 1.

In molecules such as $C_2B_3H_7$ it can be recognized that there are extra hydrogens, extra in the sense that there are more hydrogens than necessary for each vertex atom to have one exopolyhedral hydrogen atom. Extra hydrogens are generally regarded as contributing to the framework electron count. Usually extra hydrogens are found at open, or nontrigonal, faces of deltahedral-fragments in the form of bridging hydrogens in B–H–B groups or as second hydrogen atoms in BH_2 groups. Both of these types of hydrogen locations are reminiscent of framework positions in that the bridge positions usually reside close to a spheroidal extension of the polyhedral surface, and in that one hydrogen of the BH_2-group is usually *endo* (close to a framework extension) and the other *exo*. In addition, extra hydrogens are often acidic and can be removed using bases to give anions, frequently without substantially altering framework geometry. In this respect, extra hydrogens may be regarded conceptually as protonated framework electrons. This concept suggests that the addition of a lone-pair donor, such as a hydride ion H^-, to a polyhedral framework adds two electrons and changes the molecule's classification accordingly.

***Arachno* Clusters ($2n + 6$ Systems).** In comparison to the number of known *closo* and *nido* boranes and heteroboranes, there are relatively fewer *arachno* species. Partly because of the lack of a large number of structures on which to base empirical rules, *arachno* structures appear to be less predictable than their *closo* and *nido* counterparts. For example, there are two isomeric forms of B_9H_{15}, one with the *arachno [19465-30-6]* framework shown in Figure 2 (33), the other with a framework more reminiscent of that shown for the nine-atom *nido* classification (34). Structures of *arachno* molecules involve the presence of even more extra hydrogens or other electron-donating heteroatoms than *nido* molecules. Typical examples are given in Table 1.

***Hypho* Clusters ($2n + 8$ Systems).** *Hypho* molecules are even more electron-rich. Members of the *hypho* class are fairly rare and therefore examples of their structures have not been included in Figure 2. $B_5H_9[P(CH_3)_3]_2$ *[39661-74-0]*, $[B_5H_{12}]^-$; *[11056-98-7]*, and $B_5H_{10}[P(CH_3)_3]_2$ *[57034-29-4]*, three molecules that contain $2n + 8$ framework electrons and that represent members of the *hypho* class of boron hydrides, have been prepared and structurally characterized (35). As expected, this class adopts structures that are more open than their *arachno* and *nido* counterparts. The structure of $B_5H_9[P(CH_3)_3]_2$ is illustrated in Figure 3. In this *hypho* molecule there are two nonbonding basal B–B distances (those not bridged by hydrogen). In *arachno*-B_5H_{11} *[18433-84-6]* there is only one nonbonding basal B–B distance and in *nido*-B_5H_9 *[19624-22-7]* all basal distances of the pyramid are bonding (see the $n = 5$ horizontal row of Fig. 2). Another example of a *hypho* molecule is $B_4H_8[P(CH_3)_3]_2$ *[66750-83-2]* (36).

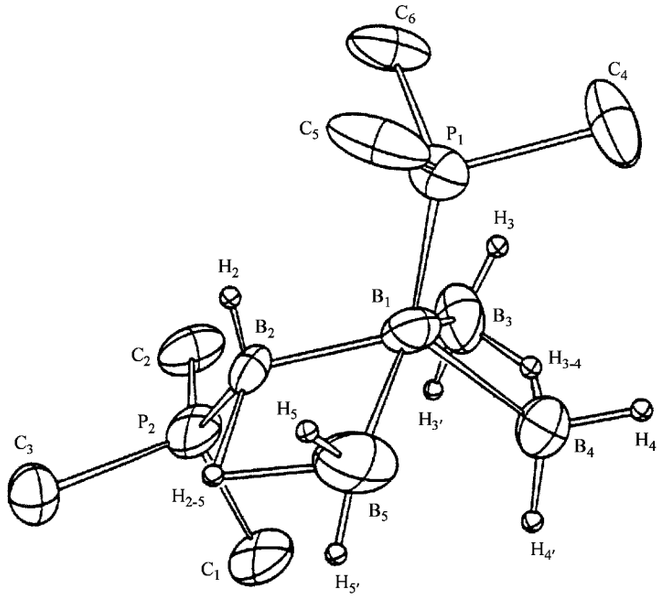


Fig. 3. The *hypho* molecule $B_5H_9[P(CH_3)_3]_2$.

Courtesy of the American Chemical Society.

Metalla Derivatives. Compounds formed from main group metals and borane or heteroborane cages can be treated using the electron-counting systematics described. For example, the metallacarborane complexes *closo*-$MC_2B_9H_{11}$ (M = Ge *[27071-59-9]*, Sn *[23151-46-4]*, Pb *[27071-51-8]*) may be regarded as tricarbaborane analogues in which the Group 14 metals are present as bare vertices (37). The metals in these clusters in theory possess a nonbonding lone pair of electrons (38) and contribute their remaining two valence electrons to the framework to give a 26-electron *closo* icosahedron.

In addition to satisfying the framework electron requirements of the cage, transition-metal metallaboranes and metallaheteroboranes also generally adhere to the eighteen electron rule, and therefore require a somewhat different electron accounting treatment. Assuming that the metal vertex uses only three orbitals in cluster bonding, then 12 of the 18 valence electrons available at a metal vertex are not involved in cluster bonding. Thus the metal *d*-electrons may effectively be treated as not included as framework electrons. These premises have been generalized to give the number of skeletal electrons per metal vertex as $(v + x - 12)$, where v is the number of valence electrons of the metal and x is the number of electrons donated by exopolyhedral substituents and ligands (39). In this formalism, moieties such as $(CO)_3Fe$ and $(\eta^5\text{-}C_5H_5)Co$ can be regarded as donating two electrons to cage bonding and are analogous to a B–H vertex. In the same way, the $(\eta^5\text{-}C_5H_5)Ni$ moiety functions as a three-electron donor vertex analogous to a C–H vertex. Other examples of common vertex groups and their electron contributions to framework bonding are given in Table 2 (14) and Figure 4. The extension of these principles to organometallics is straightforward: $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ and $(C_5H_5)Co(CO)_3$ may be considered to be *nido* and *arachno* species, respectively, as indicated in Figure 4.

Table 2. Framework Electron Contributions for Metal Moieties[a]

Metal (M)	v	$M(CO)_2$ $x = 4$	$M(\eta^5\text{-}C_5H_5)$ $x = 5$	$M(CO)_3$ $x = 6$
Cr	6	(−2)	(−1)	0
Mn	7	(−1)	0	1
Fe	8	0	1	2
Co	9	1	2	3
Ni	10	2	3	4

[a] The general contribution for a metal with v valence electrons and exopolyhedral ligands donating x electrons is $v + x - 12$ framework electrons. See text.

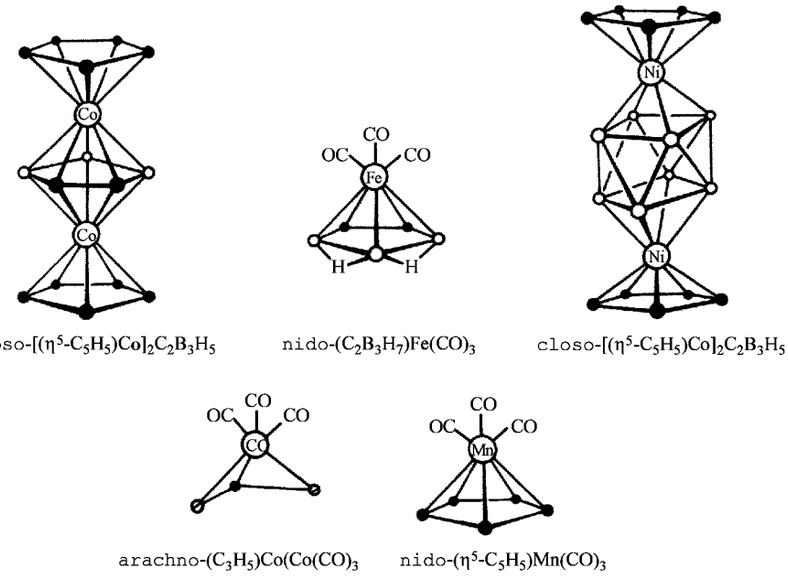


Fig. 4. Metallaboranes and organometallics of the *closo*, *nido*, and *arachno* classification. ○, BH; ●, CH; Φ, CH_2.

Placement of Heteroatoms. Many of the deltahedra and deltahedral fragments of Figure 2 have two or more nonequivalent vertices. Nonequivalent vertices are recognized as having a different order; ie, a different number of nearest neighbor vertices within the framework. Heteroatoms generally exhibit a positional preference based on the order of the polyhedral vertex and the electron richness of the heteroatom relative to boron. Electron-rich heteroatom groupings contribute more framework electrons than a :B–H moiety, which has two framework electrons, and generally appear to prefer low order vertices, ie, those having fewer neighbors. For example, two of the three isomeric forms of $C_2B_8H_{10}$ can be isomerized thermally to the 1,10-isomer *[13653-23-8]* (19), the molecule with the carbons at the lowest order vertices. The pyrolysis of *nido*-6-SB_9H_{11} *[59120-72-8]* gives *closo*-1-SB_9H_9 *[41646-56-4]*, with sulfur at the lowest order vertex (22) (see Fig. 1 for numbering conventions). When the heteroatom is in the same group as boron it preferably adopts a high order vertex; eg, $CH_3GaC_2B_4H$ *[36607-02-2]* (18). The transition-metal moieties occur predominantly at high order vertices. The carborane *nido*-1,2-dicarbapentaborane *[26249-71-8]*, $C_2B_3H_7$, presents a notable exception to the predilection of the carbon for low order vertices. It has been suggested that this exception is related to the placement of bridge hydrogens on the open face (10).

Placement of Extra Hydrogens. The placement of extra hydrogens plays a crucial role in determining the structures adopted by boranes and carboranes. However, the exact position of extra hydrogens sometimes depends on the physical state of the molecule, eg, the tridecahydrodecaborate(1) anion, $[B_{10}H_{13}]$; *[36928-50-4]* exhibits different bridge hydrogen placements in the crystal (40) and in solution (41) as can be inferred from experimental evidence, but the solution data are also consistent with a dynamic process of bridge hydrogen tautomerism. A well-documented example of fluxionality for bridge hydrogens is provided by B H_{10} (42). In spite of the controversy regarding hydrogen placement in certain boranes, some empirical rules are evident: (*1*) bridging hydrogens generally occur only between two adjacent boron atoms at an open nontriangular face of the skeleton, and only occasionally bridging a triangular array of borons (43); (*2*) when possible, the bridge termini are the low order vertices of the open face; and (*3*) there is only one bridging hydrogen per edge. Generally, BH_2 groups may be postulated as tautomeric intermediates in fluxional *nido* boranes, but they occur as ground state moieties in *arachno* molecules and then at vertices of order three or lower. In the metallaboranes, hydrogen atoms often bridge between boron and a metal.

The placement of bridge hydrogens may be the most important variable in the determination of relative isomer stabilities, outranking placement of heteroatoms (10). A number of cases exist where heteroatoms adopt high order vertices in deference to bridge hydrogen placement at low order vertices, for example, in *nido*-1,2-$C_2B_3H_7$ one of the carbon atoms is at an unanticipated high order vertex, apparently because of bridge hydrogen atom placement (44,45).

M–H–B Bridges. Numerous metallaboranes and metallaheteroboranes are known to contain hydrogens bridging between a metal atom and a skeletal boron atom, but complexes containing covalently bound tetrahydroborate(1) *[16971-29-2]*, $[BH_4]$;, constitute the prototypical class (46). Metal tetrahydroborates have been reviewed (47). Polyboranes coordinate through bridge hydrogens in a variety of ways as shown in Figure 5. Although the bonds utilize B–H hydrogens in bridging to the metal just as for the tetrahydroborates, the presence of the cage atoms affords distinctly different structural possibilities. The B–H can be regarded as a two-electron donor to metals and often plays a role similar to that of CO in metal carbonyls to stabilize clusters.

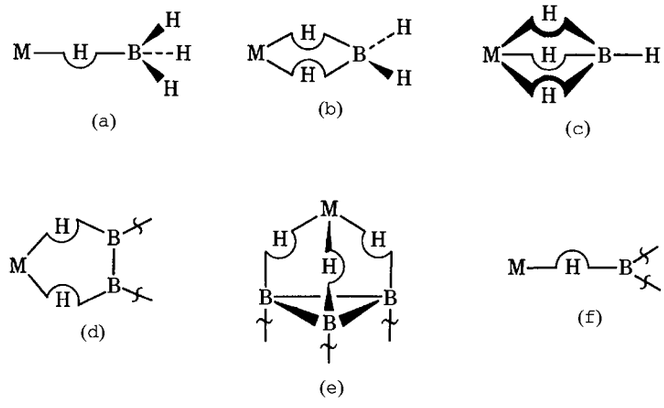


Fig. 5. Modes of M–H–B bonding where M–H–B represents a three-center hydrogen bridge bond for (**a**), (**b**), (**c**) tetrahydroborates and for (**d**), (**e**), (**f**) polyhedralboranes.

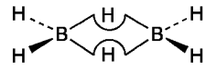
Exceptions to Structural Systematics. When strong electron-donating or -withdrawing groups are present as substituents attached to boron in polyboranes, there is the possibility of structural anomalies. In some cases electron deficiency of boron apparently can be ameliorated by back-donation instead of by the multicenter bonding afforded in a cage framework. Thus it has been suggested that exceptions to the electron-counting paradigms may occur where back-donation from the substituent to a cluster boron is possible. For example, although C_4B_2H *[12403-20-2]* has a pyramidal *nido* geometry, the structural evidence for $C_4B_2F_2H_4$ *[20534-09-2]* favors a planar form where B–H has been replaced by B–F (48).

Some metallacarboranes present anomalies to the electron-counting formalisms. Symmetrical $[commo\text{-}3,1,2\text{-}M^{n+}(C_2B_9H_{11})_2]^{n-4}$; sandwich complexes of the d metals, where M is Fe^{2+} *[51868-94-1]* and Co^{3+} *[11078-84-5]* fit the paradigm nicely (49). However, the corresponding d^8 complexes, where M is, for example, Cu^{3+} *[15721-63-8]* or Ni^{2+} *[36733-09-2]*, might be expected to show an unsymmetrically distorted partially open structure. However, symmetrically "slipped" sandwich structures are observed, suggestive of electron delocalization. The slipped structure can be explained in terms of a reduction of the *closo* molecule with a concomitant distortion as observed for *closo* carboranes (48–50). In accord with these ideas, the d^9 copper (II) complex is opened slightly more than the d^8 complex (49) and this distortion can be rationalized in terms of Jahn-Teller arguments (51). Alternatively, it is sometimes more satisfactory to view borane and carborane cages in their metal complexes as donor ligands that coordinate to metals in an appropriate fashion to contribute the number of electrons required by the specific metal center to produce a filled shell. For example, the $[nido\text{-}7,8\text{-}C_2B_9H_{11}]^{2-}$ cage can generally be regarded as a two-, four-, or six-electron donor when bound to transition metals in the η^1, η^3, or η^5 bonding modes, respectively. The η^3 π-bonding mode, which can be considered to occur in the d^8 metal complexes, involves the B_3 set of the five-membered carborane cage face and produces complexes that may be considered analogous to the well-known metal allyl complexes of traditional organometallic chemistry.

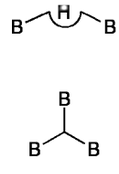
Because the electron-counting paradigm incorporates the 18-electron rule when applied to transition-metal complexes, exceptions can be expected as found for classical coordination complexes. Relatively minor exceptions are found in $(\eta^5\text{-}C_5H_5)_2Fe_2C_2B_8H_8$ *[54854-86-3]* (52) and $[Ni(B_{10}H_{12})_2]^{2-}$; *[11141-32-5]* (53). The former (2*n* electrons) is noticeably distorted from an idealized structure, and the latter is reminiscent of the d^8 and d^9 complexes discussed above. An extremely deficient electron count is obtained for complexes such as $[Cr(C_2B_9H_{11})_2]^-$; *[37036-06-9]*, which have essentially undistorted *closo* structures (54). Exceptional cases occur for certain other metallacarboranes that contain electron-rich d^8, d^9, and d^{10} metals. For example, electron-counting formalisms predict *closo* structures for $3\text{-}[(C_2H_5)_2NCS_2]\text{-}3,1,2\text{-}AuC_2B_9H_{11}$ *[62572-50-3]* (55) and $8,8\text{-}[(CH_3)_3P]_2\text{-}7,8,10\text{-}Pt\text{-}C_2B_8H_{10}$ *[58348-40-6]* (56), but *nido* structures are observed by x-ray crystallography. In some cases, ambiguities arise because bridging hydrogen atoms have not been observed in x-ray crystallographic studies.

Bonding

Localized Bonds. Because boron hydrides have more valence orbitals than valence electrons, they have often been called electron-deficient molecules. This electron deficiency is partly responsible for the great interest surrounding borane chemistry and molecular structure. The structure of even the simplest boron hydride, diborane(6) *[19287-45-7]*, B_2H_6, was sufficiently challenging that it was debated for years before finally being resolved (57) in favor of the hydrogen bridged structure shown.



The elucidation of the structure of diborane(6) led to the description of a new bond type, the three-center bond, in which one electron pair is shared by three atomic centers (58). The delocalization of a bonding pair over a three-center bond allows for the utilization of all the available orbitals in an electron-deficient system. This key point led to the formulation of a valence–bond description of the bonding in boron hydrides, sometimes termed a topological description (59). The valence structures of this topological approach give localized bonding descriptions which include delocalized three-center bonds in the basis set of bond types. In addition to the B–H–B three-center bridge bond depicted, a B–B–B three-center bond was introduced to describe bonding in the framework.



The valence theory (4) includes both types of three-center bonds shown as well as normal two-center, B–B and B–H, bonds. For example, one resonance structure of pentaborane(9) is given in projection in Figure 6. An octet of electrons about each boron atom is attained only if three-center bonds are used in addition to two-center bonds. In many cases involving boron hydrides the valence structure can be deduced. First, the total number of orbitals and valence electrons available for bonding are determined. Next, the B–H and B–H–B bonds are accounted for. Finally, the remaining orbitals and valence electrons are used in framework bonding. Alternative placements of hydrogen atoms require different valence structures.

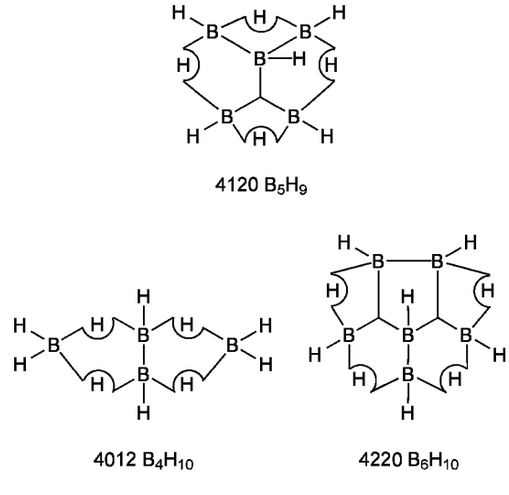


Fig. 6. The valence structures and styx numbers of B_5H_9, B_4H_{10}, and B_6H_{10}.

The possible number of valence structures for a given boron hydride has been defined exactly using three general equations of balance. For a borane of composition $[B_pH_{q+p+d}]^c$, where c is the charge, the equations are

$$s + x = q + c \tag{1}$$

$$s + t = p + c \tag{2}$$

$$t + y = p - c - \frac{1}{2}q \tag{3}$$

where p is the number of terminal B–H units, s is the number of B–H–B three-center bonds, t is the number of B–B–B three-center bonds, y is the number of B–B bonds, and x is the number of BH_2 groups. There are usually several possible solutions to the equations of balance differentiated by a so-called styx number, a four-digit number which gives the respective values of s, t, y, and x. The two-dimensional representation of B_5H_9 shown in Figure 6 has the styx number 4120. Representations of B_4H_{10} and B_6H_{10}, also shown in Figure 6, have styx numbers of 4012 and 4220, respectively. The styx formalism is equally applicable to carboranes and carbocations.

The correct styx number reflects the true molecular geometry, but the other styx structures may be transition states for fluxional molecules. Hexaborane(10) provides an example of bridge hydrogen tautomerism which is detectable by nmr (42). The tautomerism proceeds through a 3311 valence structure in which a bridge hydrogen of 4220 ground-state has been converted to a BH_2 group. It should be noted that the sum of the digits of the styx number gives one-half of the electrons involved in framework bonding, ie, the $2n + 2$, $2n + 4$, and $2n + 6$ framework electrons of the electron-counting formalism (10,11) and the topological descriptions are intimately related. Therefore, after using the electron-counting formalism to arrive at a framework structure, a valence–bond description of the localized bonds can be determined from the styx formalism (4). The simultaneous application of these two formalism allows the prediction of rearrangement during certain reactions and the prediction of transition state structure. Significant skeletal rearrangement would not be anticipated as long as the number of skeletal electrons remained unchanged, as would be the case for both associative and dissociative electrophilic mechanisms, because H^+ is the model electrophile. For the model nucleophile H^-, associative and dissociative nucleophilic mechanisms increase and decrease the framework count, respectively, and framework rearrangement would be expected during the course of the reaction (60).

Although the styx numbers quantify the various structural features present in a compound, molecules that are closely related may have very different styx numbers. For example, $[C_2H_7]^{2+}$ and B_6H_{10} have similar structures, but styx numbers of 0260 and 4220, respectively. A simplified styx system has been introduced that solves this problem (15). In this system, the s and y of styx are added together and identified as S of Stx. This number has been termed the *Chop*-Stx number (as opposed to *Lip*-styx). It can be readily seen that compounds structurally related to B_6H_{10} have the *Chop*-Stx number 620. Although at first sight it appears that information regarding the number of B–H–B groups is lost in converting styx to *Chop*-Stx, it turns out that nothing is actually lost. This is because the styx number is always used in conjunction with an empirical formula revealing the number of B–H–B groups. For example, the formula B_6H_{10} indicates that there are four more hydrogen atoms than boron atoms and the Stx number 620 indicates that there are no ($x = 0$) BH_2 groups, therefore all extra hydrogens are present as B–H–B groups. The *Chop*-Stx numbers are very useful for making structural correlations. The cataloging of all boron hydride compounds using a ten-digit number, which includes the number of framework electrons over $2n$ (n = number of vertices), the number of boron atoms, the *Chop*-Stx number, the size of the largest open face, and the number of bridging hydrogens has also been proposed (15).

Molecular Orbital Descriptions. In addition to the localized bond descriptions, molecular orbital (MO) descriptions of bonding in boranes and carboranes have been developed (4). Early work on boranes helped develop one of the most widely applicable approximate MO methods, the extended Hückel method. Molecular orbital descriptions are particularly useful for *closo* molecules where localized bond descriptions become cumbersome because of the large number of resonance structures that do not accurately reflect molecular symmetry. Such descriptions show that the highest occupied MO (HOMO) is degenerate for most deltahedral B_nH_n molecules, but that a closed shell is obtained for the corresponding $[B_nH_n]^{2-}$ anions. After accounting for the electrons in exopolyhedral bonds, $2n + 2$ electrons remain for framework bonding giving some theoretical justification for the electron counting formalisms (10,11). Symmetry considerations (61) also give justification for the opening of *closo* boranes (62) or carboranes (44) upon addition of electrons.

The *ab initio* molecular orbital calculations for smaller boranes and carboranes has progressed to the point where definitive answers to structural problems can be provided in many cases. The correlation of experimental boron nmr chemical shifts with those calculated *ab initio* using the method known as individual gauge for localized molecular orbitals (IGLO) (63) has proven to be a valuable technique for solving structural problems. This method is especially useful when calculated chemical shifts are sensitive to geometrical changes. For example, comparison of the observed and calculated ^{11}B nmr chemical shifts for *nido*-$C_2B_6H_{10}$ strongly favors a symmetrical structure having a six-membered open face out of the three candidate structures for this compound (64). Also, the proposed existence of three separate structures for $[$*closo*-$B_8H_8]^{2-}$ anions, one in the crystal, D_{2d}, and two in solution, C_{2v} and D_{4d}, has been reinvestigated using experimental–theoretical ^{11}B nmr chemical shift comparisons (64). These studies indicated that the higher temperature solution structure of $[$*closo*-$B_8H_8]^{2-}$ anions is D_{2d}, the same as seen in the crystal, and is fluxional involving a somewhat less stable C_{2v} configuration intermediate having a square open face. The structure of the third isomer is unknown.

Boranes

***Nido* and *Arachno* Boranes.** These boranes are generally more reactive and less stable thermally than the corresponding *closo* boranes. The most extensively studied boranes include diborane(6), B_2H_6, tetraborane(10), B_4H_{10}, pentaborane(9), B_5H_9, and decaborane(14), $B_{10}H_{14}$. This subject has been reviewed (57). A great deal of early work in this area was associated with the government-sponsored high energy fuels programs. Some of this work is summarized (3). The *nido* and *arachno* boranes smaller than $B_{10}H_{14}$ are quite reactive toward oxygen and water. The properties of selected boranes are given in Table 3.

Table 3. Physical Properties of Boranes

Borane	CAS Registry Number	Molecular formula	Mp, °C	Bp, °C	ΔH_f°, kJ/mol[a]	ΔG_f°, kJ/mol[a]	ΔS_{298}°, J/(K·mol)[a]
diborane(6)	*[19287-45-7]*	B_2H_6	164.9	92.6	35.5	86.6	232.0
tetraborane(10)	*[18283-93-7]*	B_4H_{10}	120	18	66.1		
pentaborane(9)	*[19624-22-7]*	B_5H_9	46.6	48	73.2	174	275.8
pentaborane(11)	*[18433-84-6]*	B_5H_{11}	123	63	103.0		
hexaborane(10)	*[23777-80-2]*	B_6H_{10}	62.3	108	94.6		
decaborane(14)	*[17702-41-9]*	$B_{10}H_{14}$	99.7	213	31.5	216.1	353.0

[a] To convert J to cal, divide by 4.184.

Diborane(6). This compound is manufactured by Callery Chemical Co. in Callery, Pennsylvania. Laboratory-scale preparations are given in equations 4–64 5 6, of which the last may be the most convenient method. Diborane is the most important starting material for all the other boron hydrides.

$$3\ NaBH_4 + 4\ (C_2H_5)_2{\cdot}BF_3 \xrightarrow{\text{diglyme}} 2\ B_2H_6 + 3\ NaBF_4 + 4\ (C_2H_5)_2O \tag{4}$$

$$2\ NaBH_4 + H_2SO_4 \rightarrow B_2H_6 + 2\ H_2 + Na_2SO_4 \tag{5}$$

$$2\ NaBH_4 + I_2 \xrightarrow{\text{diglyme}} B_2H_4 + 2\ NaI + 2\ H_2 \tag{6}$$

It is a spontaneously flammable gas having an extremely high heat of combustion.

$$B_2H_6 + 3\ O_2 \rightarrow B_2O_3 + 3\ H_2O\ \Delta H^\circ \quad 2165\ kJmol^{-1}\ (\ 517.4\ kcal\ mol) \tag{7}$$

Only H_2, BeH_2, and $Be(BH_4)_2$ have higher heats of combustion. When diborane is pyrolyzed above 100°C in a sealed tube, it is decomposed to higher boron hydrides and hydrogen gas in a complex sequence of reactions. This reaction has been investigated in considerable detail (65).

Octahydrotriborate(1). The octahydrotriborate(1-) anion *[12429-74-2]*, $[B_3H_8^-]$, commonly referred to as the triborohydride ion, is produced by the reduction of diborane with sodium amalgam. Large quantities can be prepared more conveniently by the reaction of sodium tetrahydroborate and iodine.

$$3\ NaBH_4 + I_2 \xrightarrow[100^\circ C]{\text{diglyme}} Na[B_3H_8] + 2\ H_2 + 2\ NaI \tag{8}$$

The tetraalkylammonium salts of $[B_3H_8^-]$, formed by ion-exchange reactions, have proven to be useful synthetic reagents because of their thermal and air stabilities. The structure of the $[B_3H_8^-]$ ion has been determined by an x-ray study (66) and shown to have the 2013 styx structure, C_{2v} symmetry. Mechanisms for the formation of this ion have been proposed (67). Tetraborane(10) can be easily obtained from salts of $[B_3H_8^-]$ (eq. 9).

$$4\ HCl + 4\ Na[B_3H_8] \rightarrow 3\ B_4H_{10} + 4\ NaCl + 3\ H_2 \tag{9}$$

Pentaborane(9). Pentaborane(9) and $B_{10}H_{14}$ can be prepared by gas-phase pyrolysis of B_2H under different conditions. Pentaborane(9) is a low boiling and highly flammable material produced in large quantities many years ago under government research programs. Pentaborane(9) is commercially available from Callery Chemical Co. In addition to metalla derivatives, pentaborane(9) can be used to selectively prepare a number of higher boranes and carboranes (68) (eqs. 10 11 12 13). In most cases these reactions can be carried out as one-pot procedures by combining the reactions shown in equations 10 and 11 with other reactions.

$$1.8\ B_5H_9 + NaH \xrightarrow{\text{glyme}} Na[B_9H_{14}] + H_2 + \text{minor products} \tag{10}$$

$$Na[B_9H_{14}] + HCl + (C_2H_5)_2O \rightarrow B_9H_{13}{\cdot}O(C_2H_5)_2 + NaCl + H_2 \tag{11}$$

$$Na[B_9H_{14}] + BCl_3 + [(CH_3)_4N]Cl \xrightarrow[BCl_3]{\text{glyme}} B_{10}H_{14} + [(CH_3)_4N][BCl_3H] + NaCl \tag{12}$$

$$B_9H_{13}{\cdot}O(C_2H_5)_2 + 4\ HC{\equiv}CH \xrightarrow{5,6} C_2B_8H_{12} + (C_2H_5)_2O{\cdot}B(CH{=}CH_2)_3 \tag{13}$$

Decaborane(14). One of the most important and intensely studied of the polyhedral boron hydrides, this colorless, highly flammable, crystalline solid has been produced in large quantities from the 1940s to the 1970s. The most recent decaborane plant was built and operated at Callery, Pennsylvania, during the late 1970s under a government contract. Decaborane(14) can be prepared on a laboratory scale by the pyrolysis of B_2H at 100–200°C in the presence of a catalytic amount of a Lewis base such as dimethylether, $(CH_3)_2O$. In addition to the gas-phase pyrolysis of diborane, $B_{10}H_{14}$ can be prepared by a solution-phase process developed at Union Carbide Corp. Decaborane is a key intermediate in the preparation of many carboranes and metalla derivatives. As of this writing, this important compound is not manufactured on a large scale in the western world and is in short supply. Prices for decaborane in 1991 were up to $10,000 kg.

Reactions of Boranes with Lewis Bases. Boranes that contain a BH_2 moiety, eg, B_2H , B_4H_{10}, B_5H_{11}, hexaborane(12) *[28375-94-2]*, $B\ H_{12}$, and nonaborane(15) *[19465-30-6]*, B_9H_{15}, can generally be cleaved by nucleophiles in two ways termed symmetrical and unsymmetrical bridge cleavage (69). Using neutral bases the two modes of cleavage lead to molecular and ionic fragments, respectively, as illustrated in equations 14–19.

$$B_2H_6 + 2\ NH_3 \rightarrow [H_2B(NH_3)_2]^+\ (BH_4^-) \tag{14}$$

$$B_2H_6 + 2(CH_3)_2S \rightarrow 2(CH_3)_2S{\cdot}BH_3 \tag{15}$$

$$B_4H_{10} + 2\ NH_3 \rightarrow [H_2B(NH_3)_2]^+\ (B_3H_8^-) \tag{16}$$

$$B_4H_{10} + 2\ N(CH_3)_3 \rightarrow (CH_3)_3N{\cdot}BH_3 + (CH_3)_3N{\cdot}B_3H_7 \tag{17}$$

$$B_5H_{11} + 2\ NH_3 \rightarrow [H_2B(NH_3)_2]^+\ [B_4H_9^-] \tag{18}$$

$$B_5H_{11} + 2\ CO \rightarrow BH_3(CO) + B_4H_8(CO) \tag{19}$$

Certain base adducts of borane, BH_3, such as triethylamine borane *[1722-26-5]*, $(C_2H_5)_3N \cdot BH_3$, dimethylsulfide borane *[13292-87-0]*, $(CH_3)_2S \cdot BH_3$, and tetrahydrofuran borane *[14044-65-6]*, $C_4H_8O \cdot BH_3$, are more easily and safely handled than B_2H and are commercially available. These compounds find wide use as reducing agents and in hydroboration reactions (57). A wide variety of borane reducing agents and hydroborating agents is available from Aldrich Chemical Co., Milwaukee, Wisconsin. Base displacement reactions can be used to convert one adduct to another. The relative stabilities of BH_3 adducts as a function of Group 15 and 16 donor atoms are P > N and S > O. This order has sparked controversy because the trend opposes the normal order established by BF_3. In the case of anionic nucleophiles, base displacement leads to ionic hydroborate adducts (eqs. 20,21).

$$(C_2H_5)_2O{\cdot}BH_3 + KF \rightarrow K^+[BH_3F]^- + (C_2H_5)_2O \tag{20}$$

$$(C_2H_5)_2O{\cdot}BH_3 + Na(SCN) \rightarrow Na^+(BH_3SCN)^- + (C_2H_5)_2O \tag{21}$$

Unsymmetrical cleavage of B_2H by metal hydrides gives metal tetrahydroborate salts, also called metal borohydrides or hydroborates.

$$2\,MH + B_2H_6 \rightarrow 2\,MBH_4 \quad (M = Li, Na, K) \tag{22}$$

Except for $B_{10}H_{14}$, a more detailed consideration of the interaction of donor ligands with boranes is beyond the scope of this review. Decaborane is a multifunctional species that simultaneously acts as a Brønsted acid and a Lewis acid. Weak bases fail to directly deprotonate decaborane but do react resulting in the evolution of H_2 and the formation of species that contain ligands coordinated at the six- and nine-positions of the decaborane skeleton (see Fig. 1**l**).

$$B_{10}H_{14} + 2\,L \rightarrow B_{10}H_{12}L_2 + H_2 \tag{23}$$

Base displacement reactions (70) have been used to establish the relative basicities of a number of ligands toward $B_{10}H_{12}$ to be as follows: $(C_6H_5)_3P$ > pyridine > $(C_2H_5)_3N$ > $CH_3CON(CH_3)_2$ > $HCON(CH_3)_2$ > $(C_2H_5)_2NCN$ ~ CH_3CN > $(CH_3)_2S$. The $B_{10}H_{12}L_2$ species are important intermediates in the synthesis of two-key *closo* species, $[B_{10}H_{10}]^{2-}$; and 1,2-$C_2B_{10}H_{12}$.

Proton Abstraction. Although the exopolyhedral hydrogens of *nido* and *arachno* boranes are generally considered hydridic, the bridge hydrogens are acidic as first demonstrated by titration of $B_{10}H_{14}$ and deuterium exchange (71). Some typical reactions are

$$B_{10}H_{14} + NaOH \rightarrow Na^+[B_{10}H_{13}]^- + H_2O \tag{24}$$

$$B_{10}H_{14} + NaH \rightarrow Na^+[B_{10}H_{13}]^- + H_2 \tag{25}$$

$$B_5H_9 + n\text{-}C_4H_9Li \rightarrow Li^+[B_5H_8]^- + C_4H_{10} \tag{26}$$

$$B_4H_{10} + NaH \rightarrow Na^+[B_4H_9]^- + H_2 \tag{27}$$

$$B_6H_{10} + KH \rightarrow K^+[B_6H_9]^- + H_2 \tag{28}$$

The deprotonation of $B_{10}H_{14}$ at a B–H–B bridge position produces the yellow species $[B_{10}H_{13}]^-$; (72–75). Reaction of the $[B_{10}H_{13}]^-$ anion and an electron-pair donor L, produces $[B_{10}H_{13}L]^-$; (76). Hydration of $B_{10}H_{14}$ results in the acidic species $B_{10}H_{14}OH_2$, which ionizes to form the colorless $[B_{10}H_{14}OH]^-$ anion (75). Both $B_{10}H_{14}OH_2$ and $[B_{10}H_{14}OH]^-$ are isoelectronic with the $[B_{10}H_{15}]^-$ anion (77). The hydropolyborate ions formed by proton abstraction from decaborane are useful intermediates for the preparation of metallaboranes and heteroboranes.

Polyhedral Expansion. The term polyhedral expansion is used to describe a host of reactions in which the size of the polyhedron is increased by the addition of new vertex atoms whether boron, heteroelements, or metals. In the case of the boranes, the pyrolysis of B_2H has been used to obtain B_5H_9 and $B_{10}H_{14}$ industrially. Although a subject of much study, the mechanism of such pyrolytic expansions is not well understood.

Expansion of $B_{10}H_{14}$ to $[B_{11}H_{14}]^-$ is brought about by a reaction with $[BH_4]^-$ (78).

$$[BH_4]^- + B_{10}H_{14} \rightarrow [B_{11}H_{14}]^- + 2\,H_2 \tag{29}$$

Other expansion reactions between diborane and borane anions with a B—B edge bond have been reported (79), for example

$$2[B_4H_9]^- + B_2H_6 \rightarrow 2(B_5H_{12}^-) \tag{30}$$

$$2[B_5H_8]^- + B_2H_6 \rightarrow 2[B_6H_{11}]^- \tag{31}$$

Boron halides have also been shown to insert into B—B bonds to give initial products with the new boryl moiety in a bridge position (80).

$$(B_5H_8)^- + (CH_3)_2BCl \rightarrow \mu\text{-}[(CH_3)_2B]\text{-}B_5H_8^- + Cl^- \tag{32}$$

$$\mu\text{-}[(CH_3)_2B]\text{-}B_5H_8 \xrightarrow{(C_2H_5)_2O} (CH_3)_2B_6H_8 \tag{33}$$

Electrophilic Attack. A variety of boranes, heteroboranes, and metallaboranes undergo electrophilic substitution. Susceptibility of boranes to electrophilic attack is often detected by deuteron–proton exchange experiments. For example, electrophilic hydrogen–deuterium exchange of $B_{10}H_{14}$ occurs at the 1-,2-,3-, and 4-positions when exposed to DCl in the presence of $AlCl_3$ (81). The trend to increasing positive sites in $B_{10}H_{14}$ is $2,4 < 1,3 < 5,7,8,10 < 6,9$. Initial halogenation and alkylation of $B_{10}H_{14}$ also occurs at the 2,4-positions (81,82). Electrophilic substitution of pentaborane(9) has also been observed to give halogenation, alkylation, and deuteration. The more negative apical site (1-position) is substituted preferentially, but the 1-isomer can be catalytically converted to the basally substituted isomer (2-position) (83) (Fig. 1**b**). The basal B—B bond of B_5H_{10}

can be protonated to give the isolable polyhedral borane cation, $[B_{11}H_{11}]^+$ (84) (Fig. 1**d**).

***Closo* Borane Anions.** This group contains a homologous series of very stable polyhedral anions, $[closo\text{-}B_nH_n]^{2-}$, $n = 6-12$. Just as the previously known boron hydrides might be considered as analogues of aliphatic hydrocarbons, the *closo* borane anions are analogues of aromatic hydrocarbons. The stability of the *closo* anions is attributable to electron delocalization in a unique three-dimensional aromaticity. Unlike their *nido* and *arachno* counterparts with bridging hydrogens, proton abstraction does not, for practical purposes, occur in *closo* borane chemistry. Instead, acid catalysis is important in their substitution chemistry. The best known members of this series, $[closo\text{-}B_{10}H_{10}]^{2-}$ *[12356-12-6]* and $[closo\text{-}B_{12}H_{12}]^{2-}$ *[12356-13-7]*, were first reported in 1959 and 1960 (85) and were the subject of detailed studies (86).

In aqueous solution, *closo* borane anions are very stable as their conjugate acids, which possess acidity similar to sulfuric acid, yet their chemistry is remarkably different. Large unipositive cations, such as Tl^+, Cs^+, Rb^+, $[(CH_3)_4N]^+$, and $[(CH_3)_3S]^+$, yield water-insoluble salts of $[B_{12}H_{12}]^{2-}$ and $[B_{10}H_{10}]^{2-}$ (87). Small unipositive cations and most dipositive cations, such as Ba^{2+} and Ca^{2+}, form water-soluble salts that are strong electrolytes and give hydrates on evaporation. The divalent transition and rare-earth elements also give soluble salts and hydrates, but solubilities decrease when the water of the coordination sphere is replaced by ligands such as NH_3. Polarizing cations, such as Ag^+, Cu^+, Tl^+, and Hg^{2+} form water-insoluble salts. The latter compounds contain M–H–B interactions in the solid state. Salts of cations, which are not readily reducible, display exceptional thermal stabilities. Thus $Cs_2[B_{12}H_{12}]$ and $Cs_2[B_{10}H_{10}]$ can be heated to 810 and 600°C, respectively, in a sealed, evacuated tube and recovered unchanged.

Salts of $[B_{12}H_{12}]^{2-}$ *[12429-97-9]*, $[B_7H_7]^{2-}$ *[12430-07-8]*, $[B_8H_8]^{2-}$ *[12430-13-6]*, $[B_9H_9]^{2-}$ *[12430-00-0]*, and $[B_{11}H_{11}]^{2-}$ *[12430-44-3]* appear to exhibit similar behavior, but less definitive data are available. Although silver salts of $[B_{12}H_{12}]^{2-}$, $[B_9H_9]^{2-}$, and $[B_{11}H_{11}]^{2-}$ have been isolated, they are shock-, heat-, and light-sensitive (88,89). Anhydrous $Cs_2[B_{12}H_{12}]$, $Cs_2[B_8H_8]$, and $Cs_2[B_9H_9]$ are thermally stable to 600°C, but $Cs_2[B_{11}H_{11}]$ disproportionates to $Cs_2[B_{10}H_{10}]$ and $Cs_2[B_{12}H_{12}]$ at temperatures above 400°C (17).

The base-promoted closure of decaborane(14) yields salts of the $[B_{10}H_{10}]^{2-}$ anion (eq. 34). Relatively strong Lewis bases, such as trialkylamines, are required to accomplish this reaction as weaker bases, such as diethylsulfide and acetonitrile, form stable 6,9-$L_2B_{10}H_{12}$ species where L = $(C_2H_5)_2S$, H_3CCN, etc (90).

$$B_{10}H_{14} + 2\,N(C_2H_5)_3 \xrightarrow{-H_2} 6,9\text{-}[(C_2H_5)_3N]_2[B_{10}H_{12}] \rightarrow [(C_2H_5)_3NH]_2[B_{10}H_{10}] + H_2 \quad (34)$$

The reaction of B_2H_6 with $NaBH_4$ or $(C_2H_5)_3N{\cdot}BH_3$ at 180°C in $N(C_2H_5)_3$ at high pressure gives $[B_{12}H_{12}]^{2-}$ in nearly quantitative yield (91). In diglyme at 162°C, the same reactants give a 5–10% yield of $[B_{12}H_{12}]^{2-}$; at even lower (85°C) temperatures and at atmospheric pressure $Na[B_3H_8]$ *[12429-74-2]* is obtained (89,92).

$$2\,NaBH_4 + 5\,B_2H_6 \rightarrow Na_2[B_{12}H_{12}] + 13\,H_2 \quad (35)$$

$$2[(C_2H_5)_3N]BH_3 + 5\,B_2H_6 \rightarrow [(C_2H_5)_3NH]_2[B_{12}H_{12}] + 11\,H_2 \quad (36)$$

Pyrolysis of $Cs[B_3H_8]$ at 230°C gives $Cs_2[B_9H_9]$ (60%) along with some $Cs_2[B_{10}H_{10}]$, $Cs_2[B_{12}H_{12}]$, and $CsBH_4$ (93). The sensitivity of polyhedral expansion reactions to solvent, temperature, and pressure is further exemplified by the results in dioxane at 120°C under pressure. To obtain the *closo* borane, $Na[B_{11}H_{14}]$ is first converted to $Cs_2[B_{11}H_{13}]$, which can be pyrolyzed to give $Cs_2[B_{11}H_{11}]$ (89).

$$NaBH_4 + 5\,B_2H_6 \xrightarrow{120^\circ C} Na[B_{11}H_{14}] + 10\,H_2 \quad (37)$$

Pyrolysis of $[(C_2H_5)_4N][BH_4]$ at 185°C gives a 90% yield of $[(C_2H_5)_4N]_2[B_{10}H_{10}]$ (94). The $[B_{12}H_{12}]^{2-}$ anion can be prepared by the reaction of $(C_2H_5)_3N{\cdot}BH_3$ with decaborane in an inert high boiling hydrocarbon solvent at 190°C (92).

$$2[(C_2H_5)_3N]BH_3 + B_{10}H_{14} \xrightarrow{190^\circ C} [(C_2H_5)NH]_2[B_{12}H_{12}] + 3\,H_2 \quad (38)$$

The $[B_{12}H_{12}]^{2-}$, $[B_7H_7]^{2-}$, $[B_8H_8]^{2-}$, $[B_9H_9]^{2-}$, and $[B_{11}H_{11}]^{2-}$, *closo* anions are hydrolytically less stable than the $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ *closo* anions. All of these anions are more stable in basic than in acidic solution. $[B_7H_7]^{2-}$ is the least stable hydrolytically and is degraded even in basic media. The $[B_{12}H_{12}]^{2-}$, $[B_8H_8]^{2-}$, and $[B_9H_9]^{2-}$ *closo* anions are stable in neutral and alkaline solutions but react rapidly with aqueous acid. Strongly acidic solutions (>2*N* HCl) are necessary for the hydrolysis of $[B_{11}H_{11}]^{2-}$. The $[B_{12}H_{12}]^{2-}$ anion is the most hydrolytically stable borane anion, withstanding even 3 *N* HCl at 95°C, conditions that slowly degrade $[B_{10}H_{10}]^{2-}$ (17,88).

Nucleophilic substitution chemistry of the $[closo\text{-}B_nH_n]^{2-}$ anions are not well understood. In the cases where $n = 10, 12$, reactions can be described as acid-catalyzed nucleophilic substitution. Most acid-catalyzed nucleophilic substitutions of $[B_{10}H_{10}]^{2-}$ with, for example, amides, ethers, and sulfones give products having equatorial substituents.

$$(B_nH_n)^{2-} + 2\,R_2O \rightarrow [B_nH_{n-2}(OR)_2]^{2-} + RH \quad (39)$$

$$(B_nH_n)^{2-} + H^+ + HCON(CH_3)_2 \rightarrow [B_nH_{n-1}(OCH{=}N(CH_3)_2)]^- + H_2 \quad (40)$$

$$[B_nH_n]^{2-} + H^+ + R_2SO_2 \rightarrow [B_nH_{n-1}OS(O)R_2]^- + H_2 \quad (41)$$

These *O*-bonded substituents are easily cleaved with hydroxide ion to give the corresponding hydroxyl derivative, $[B_nH_{n-1}(OH)]^{2-}$ or $[B_nH_{n-2}(OH)_2]^{2-}$, $n = 10, 12$. Halogenation of $[B_{12}H_{12}]^{2-}$ by HCl and HF has been termed acid-catalyzed nucleophilic attack (95).

The reaction of $[B_{10}H_{10}]^{2-}$ with excess nitrous acid gives an explosive intermediate that can be reduced to the nonexplosive bis inner diazonium salt 1,10-$(N_2)_2B_{10}H_8$ *[66750-86-5]* (eq. 42). This diazonium species is a useful synthetic intermediate.

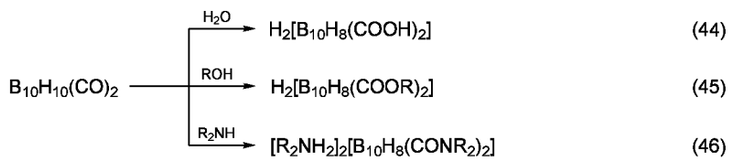
$$[B_{10}H_{10}]^{2-} \xrightarrow{HONO} [\text{explosive intermediate}] \xrightarrow{Na[BH_4]} 1,10\text{-}(N_2)_2B_{10}H_8$$

Unfortunately, $[B_{12}H_{12}]^{2-}$ does not undergo the corresponding reaction. Nitrogen is the only ligand that can be displaced from the B_{10}-cluster by a variety of nucleophiles (96).

$$1,10-(N_2)_2B_{10}H_8 + 2L \rightarrow 1,10-L_2B_{10}H_8 + 2N_2 \tag{43}$$

where L ammonia, amines, nitriles, hydrogen sulfide, azide ion, hydroxide ion, and carbon monoxide.

The dicarbonyl *[12539-66-1]* available from 1,10-$(N_2)_2B_{10}H_8$ is another important species because of the scope of its chemistry. Carbonyls of $[B_{12}H_{12}]^{2-}$ can be formed from CO and the conjugate acid of $[B_{12}H_{12}]^{2-}$. The B_{10}- and B_{12}-carbonyls exhibit very similar reactivity (99). The carbonyls can be considered anhydrides of carboxylic acids and accordingly react with alcohols and amines-to give esters and amides:



(44)

(45)

(46)

Halogenation of $[B_{12}H_{12}]^{2-}$ and $[B_{10}H_{10}]^{2-}$ occurs using elemental halogen in solvents such as water, alcohols, or tetrachloroethane. Initial rates are extremely high in all cases with $[B_{10}H_{10}]^{2-} > [B_{12}H_{12}]^{2-}$. The kinetic order is F > Cl > Br > I, but F_2 causes degradation (98). Typical products are $[B_{10}Cl_{10}]^{2-}$ *[12430-33-0]*, $[B_{10}H_3Br_7]^{2-}$ *[12360-16-6]*, $[B_{10}I_{10}]^{2-}$ *[12430-43-2]*, $[B_{12}ClH_{11}]^{2-}$ *[12430-46-5]*, $[B_{12}H_3BrCl_8]^{2-}$ *[12536-79-7]*, and $[B_{12}I_{12}]^{2-}$ *[12587-25-6]*. In general, the alkali and alkaline-earth metal salts of the B_{10}- and B_{12}-halogenated derivatives have excellent thermal, oxidative, and hydrolytic stabilities.

Oxidative degradation of $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ to boric acid is extremely difficult and requires Kjeldahl digestion or neutral permanganate. The heat of reaction obtained from the permanganate degradation leads to a calculated heat of formation for $[B_{10}H_{10}]^{2-}$ (aq) of 92.5 ± 21.1 kJ mol (22.1 ± 5.0 kcal mol) (99). The oxidative coupling of both $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ has been studied in some detail (100).

The $[B_{10}H_{10}]^{2-}$ anion can be oxidized chemically or electrochemically to give $[B_{20}H_{19}]^{3-}$ and $[B_{20}H_{18}]^{2-}$ *[59724-35-5]* (eqs. 47–49).

$$(B_{10}H_{10})^{2-} \rightleftharpoons (B_{10}H_{10}) + e \tag{47}$$

$$2(B_{10}H_{10}) \rightarrow (B_{20}H_{19})^{3-} + H^+ \tag{48}$$

$$(B_{20}H_{19})^{3-} \rightarrow (B_{20}H_{18})^{2-} + H^+ + 2e \tag{49}$$

These are conjuncto-boranes consisting of two B_{10}-clusters linked via a double three-center B–B–B bond as originally proposed (101) and later confirmed by x-ray crystallography (102). The structure of $[B_{20}H_{18}]^{2-}$ is shown in Figure 7. Reduction of $[B_{20}H_{18}]^{2-}$ by sodium metal in liquid ammonia gives $[B_{20}H_{18}]^{4-}$; *[59724-36-6]*, in which the two B_{10}-clusters are joined by a single two-center B–B bond through the apical or equatorial positions. The nondestructive electrochemical oxidation of $[B_{12}H_{12}]^{2-}$ leads to the $[B_{24}H_{23}]^{2-}$ anion (103).

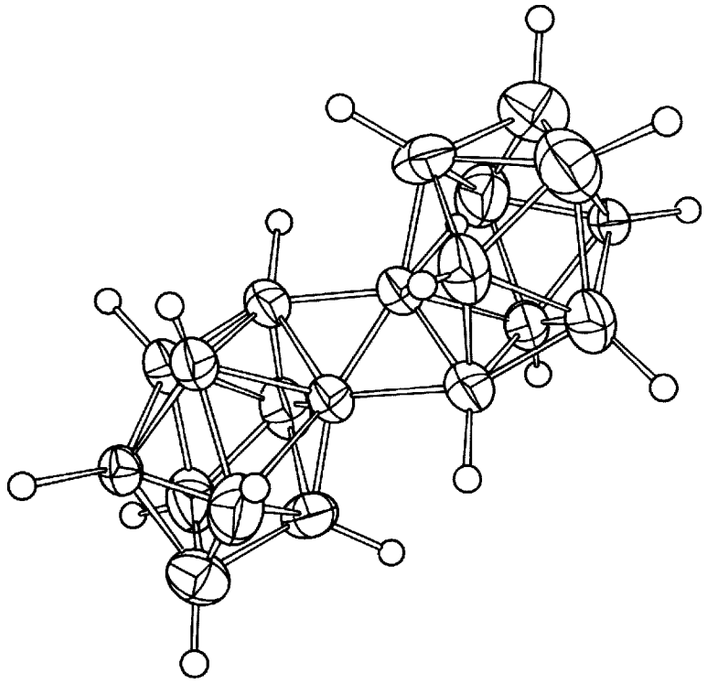


Fig. 7. The structure of $[B_{20}H_{18}]^{2-}$ where ⊕ and ○ represent B and H, respectively.

Courtesy of the American Chemical Society (102).

Tetrahydroborates. The tetrahydroboranes constitute the most commercially important group of boron hydride compounds. Tetrahydroborates of most of the metals have been characterized and their preparations have been reviewed (46). The important commercial tetrahydroborates are those of the alkali metals. Some properties are given in Table 4.

Table 4. Properties of Alkali Metal Tetrahydroborates

Property	Compound					References
	$LiBH_4$	$NaBH_4$	KBH_4	$RbBH_4$	$CsBH_4$	
CAS Registry Number	*[16949-15-8]*	*[16940-66-2]*	*[13762-51-1]*	*[20346-99-0]*	*[19193-36-3]*	
mp, °C	268	505	585			104–106
decomp. temp., °C	380	315	584	600	600	104–106
density, g mL	0.68	1.08	1.17	1.71	2.40	105,107,108
refractive index		1.547	1.490	1.487	1.498	109
lattice energy, kJ mol[a]	792.0	697.5	657	648	630.1	105
ΔH_f°, kJ mol[a]	184	183	243	246	264	108,110
ΔS_{298}°, J (mol·K)[a]	128.7	126.3	161	179	192	111

[a] To convert J to cal, divide by 4.184.

Sodium borohydride is manufactured by Morton International, Inc. Treatment of trimethyl borate with a metal hydride, eg, NaH, in the absence of a solvent yields sodium hydrotrimethoxyborate *[16940-17-3]*, $Na[HB(OCH_3)_3]$, (eq. 50) which disproportionates in the presence of solvents such as tetrahydrofuran at 60–70°C (eq. 51) (112).

$$MH + B(OCH_3)_3 \rightarrow M[BH(OCH_3)_3]\ M = Li, Na, K \tag{50}$$

$$4\ M[BH(OCH_3)_3] \rightarrow MBH_4 + 3\ M[B(OCH_3)_4] \tag{51}$$

Addition of diborane (eq. 52) under the latter conditions renders the production of MBH_4 essentially continuous until consumption of the metal hydride is complete because trimethyl borate is regenerated.

$$3\ M[B(OCH_3)_4] + 2\ B_2H_6 \rightarrow 3\ MBH_4 + 4\ B(OCH_3)_3 \tag{52}$$

This method has been used for the commercial production of $NaBH_4$, but is less satisfactory for the manufacture of $LiBH_4$ and KBH_4. Some metathetical conversions are shown in equations 53–58.

$$TlNO_3 + KBH_4 \xrightarrow{H_2O} TlBH_4 + KNO_3 \tag{53}$$

$$NaBH_4 + KOH \xrightarrow{H_2O} KBH_4 + NaOH \tag{54}$$

$$[(C_6H_5)_4P]F + KBH_4 \xrightarrow{H_2O} [(C_6H_5)_4P][BH_4] + KF \tag{55}$$

$$NaBH_4 + LiCl \xrightarrow{\text{isopropylamine}} LiBH_4 + 2\ LiCl \tag{56}$$

$$MgCl_2 + 2\ NaBH_4 \xrightarrow{\text{ethanol}} Mg[BH_4]_2 + 2\ NaCl \tag{57}$$

$$NH_4F + NaBH_4 \xrightarrow{NH_3} NH_4[BH_4] + NaF \tag{58}$$

The physical and chemical properties of the tetrahydroborates show more contrasts than the salts of nearly any other anion. The alkali metal salts are the most stable. In dry air, $NaBH_4$ is stable at 300°C and *in vacuo* to 400°C with only partial decomposition. In contrast, several tetrahydroborates, including the titanium, thallium, gallium, copper, and silver salts, are unstable at or slightly above ambient temperatures. The chemical and physical properties of the tetrahydroborates are closely related to molecular structure. Sodium tetrahydroborate, which is typical of the alkali metal tetrahydroborates except for the lithium salt, has a face-centered cubic (fcc) crystal lattice which is essentially ionic and contains the tetrahedral $[BH_4]^-$ anion. The tetrahydroborates of the polyvalent metals are in many cases the most volatile derivatives of these metals known. Aluminum tris(tetrahydroborate) *[16963-07-5]*, $Al[BH_4]_3$, has a normal boiling point of 44.5°C and uranium bis(tetrahydroborate) *[33725-14-3]*, $U[BH_4]_2$, has a vapor pressure of 530 Pa (4 torr) at 61°C. Other covalent tetrahydroborates include $Be[BH_4]_2$, $Zr[BH_4]_4$, $Hf[BH_4]_4$, and $U[BH_4]_4$. These compounds contain M–H–B-type bonds. The structure of $Al[BH_4]_3$ is shown in Figure 8. The alkali metal tetrahydroborates are stable in dry air, and the sodium and potassium salts can be crystallized from aqueous solution. Alternatively, $Al[BH_4]_3$ is hydrolyzed explosively and is pyrophoric in air.

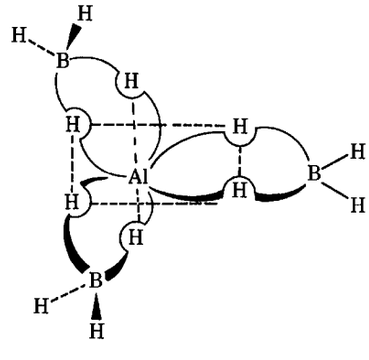


Fig. 8. The structure of $Al(BH_4)_3$.

Sodium tetrahydroborate is quite soluble in liquid ammonia and soluble to some extent in a variety of other solvents. It is appreciably soluble only in

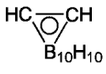
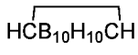
polar solvents of high dielectric constant and those which can solvate the metal ion, such as water, amines, diethylformamide, and glyme ethers. The rate of hydrolysis of $NaBH_4$ in water is increased by either lowering the pH or by increasing the temperature. It can be recrystallized from alkaline solutions. Dissolution in water results in a slow hydrolysis until the solution becomes alkaline. A 0.01 *M* solution of $NaBH_4$ gives initial pH 9.6. Only very slow hydrolysis occurs at pH values greater than 12.9.

The tetrahydroborates have been used as reducing agents for a variety of inorganic reductions. Many metal cations are reduced by tetrahydroborates in protic or aprotic solvents. The products of these reductions may be lower valent cations, free elements, volatile hydrides, or metal borides. For example, Sn, Ge, As, Sb, and Bi salts or oxides can be reduced to SnH_4, GeH_4, AsH_3, SbH_3, and BiH_3. A number of such reactions are utilized in quantitative analytical procedures. Reactive metal powder can be prepared by borohydride reduction of metal compounds such as cobalt chloride, chromium oxide, molybdenum oxide, tungsten oxide, and molybdenum oxide or chloride. Sodium tetrahydroborate, as well as amine boranes, are used in electroless plating (qv), particularly of nickel, palladium, and platinum, on both metallic and nonmetallic substrates. Many transition-metal hydride complexes have been prepared by reactions utilizing tetrahydroborates. Tetrahydroborates also find use in the bleaching of paper pulp and clays, purification of organic chemicals and pharmaceuticals, the recovery of valuable metals, and the treatment of wastewater from industrial process streams. Covalent metal tetrahydroborates derived from Ti, Zr, Co, Ni, and Rh have shown catalytic activity in hydrogenation, polymerization, and isomerization reactions (47). An important industrial use of sodium tetrahydroborate is in the production of the dithionite anion by reduction of the bisulfite anion (113).

The use of tetrahydroborates, as well as the boranes and organoboranes, for organic transformations has proven to be even more significant because these reduction reactions are highly selective and nearly quantitative (114). The reducing characteristics of borohydrides may be varied by changing the associated cation and by changing the solvent. Borohydrides are often the reagents of choice for the reduction of aldehydes and ketones to the corresponding alcohols, especially when selective reduction in the presence of other functional groups is required. Many other functional groups, such as acid chlorides, imines, and peroxides, can also be reduced using borohydrides.

Heteroboranes

Heteroboranes contain heteroelements classified as nonmetals. The heteroatoms known to form part of a borane polyhedron include C, N, Si, P, As, S, Se, Sb, and Te either alone or in combination. In principle, most heteroboranes could have a wide range of skeletal sizes. However, with the primary exception of the carbaboranes, extensive chemistry has emerged only for the thiaboranes and azaboranes, which have the greatest availability and demonstrated scope of chemistry.

Carboranes. The term carborane is widely used in American literature as a contraction of the IUPAC approved nomenclature carbaborane. The first carboranes, isomers of $C_2B_3H_5$, C_2B_4H , and $C_2B_5H_7$, were prepared in the mid-1950s at Olin Mathiesen. These carboranes were obtained as a mixture in low yield from the reaction of pentaborane(9) with acetylene in a silent electric discharge. The discovery of the icosahedral *closo*-1,2-dicarbadodecaborane(12) *[16872-09-6]*, 1,2-$C_2B_{10}H_{12}$, came soon after and led to a rapid development of carborane chemistry. This carborane, often called *ortho*-carborane, is prepared in good yields by the reaction of acetylene and one of the 6,9-$L_2B_{10}H_{12}$ species such as $[(C_2H_5)_2S]_2B_{10}H_{12}$ *[28377-92-6]* or 6,9-$(H_3CCN)_2B_{10}H_{12}$ where L a Lewis base (Fig. 9). A wide variety of *C*-substituted *ortho*-carboranes can be obtained by utilizing substituted acetylenes, RC≡CR′. The symbols  , $HCB_{10}H_{10}CH$, and  are commonly used in the literature to represent 1,2-$C_2B_{10}H_{12}$, 1,7-$C_2B_{10}H_{12}$, and 1,2-$C_2B_{10}H_{12}$, respectively. The latter two isomers, called *meta*-carborane *[16986-21-6]*, and *para*-carborane *[20644-12-6]*, respectively, are obtained by thermal isomerization (Fig. 10) of 1,12-$C_2B_{10}H_{12}$ (see Fig. 1o for the numbering convention for these icosahedral species). *C*-substituted carboranes can be obtained conveniently through the intermediacy of lithium reagents such as 1,2-dilithium-*ortho*-carborane *[22220-85-5]*, 1,2-Li_2-1,2-$C_2B_{10}H_{10}$, and 1,7-dilithium-*meta*-carborane *[17217-89-9]*, 1,7-Li_2-1,7-$C_2B_{10}H_{10}$, which are readily prepared by treatment of *o*- or *m*-carborane with *n*-C_4H_9Li. Furthermore, it has been shown (115) that 1,2-dehydro-*o*-carborane, $C_2B_{10}H_{10}$, which can be generated through loss of lithium bromide from the lithium salt of the 2-bromo-*o*-carboranyl anion, $C_2B_{10}H_{11}Br$, exhibits chemistry similar to 1,2-dehydrobenzene *[462-80-1]* (benzyne), C H_4. This reactivity was demonstrated through 2 ⊢ 2,4 ⊢ 2, and related cycloaddition reactions with dienes, leading to *C*-substituted organocyclic carboranes.

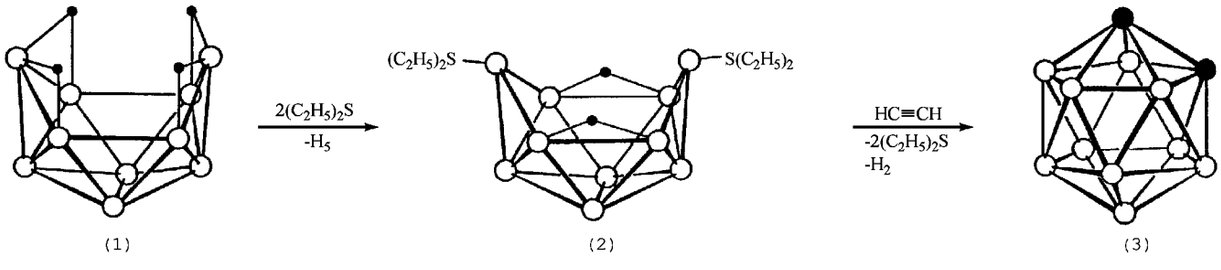


Fig. 9. The synthesis of *closo*-1,2-$C_2B_{10}H_{12}$ (**3**) from *nido*-$B_{10}H_{14}$ (**1**) via *arachno*-$[(C_2H_5)_2S]_2B_{10}H_{12}$ (**2**) where ○ represents BH; ●, CH; and ●, H.

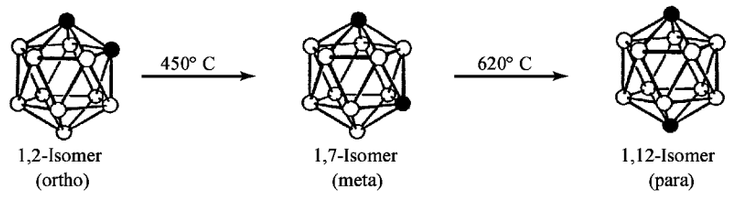


Fig. 10. Thermal rearrangement of *closo*-$C_2B_{10}H_{12}$, where ○ represents BH; ●, CH.

The discovery (116) of the base-promoted degradation of the isomeric *closo*-$C_2B_{10}H_{12}$ cages provided one of the most important carborane anion systems, the isomeric [*nido*-$C_2B_9H_{12}$] ; anions,

$$closo \quad C_2B_{10}H_{12} \vdash RO \quad \vdash 2\,ROH \quad \rightarrow [nido \quad C_2B_9H_{12}] \quad \vdash B(OR)_3 \vdash H_2 \tag{59}$$

where R = CH_3, C_2H_5, etc. The [*nido*-$C_2B_8H_{12}$] ; cages are commonly referred to as dicarbollide ions, derived from the Spanish *olla*, meaning a bowl. It should be noted that the rules governing the numbering of heteroborane cages calls for different systems for *closo* and *nido* cages (7). Thus the

base-promoted degradation of 1,2-, 1,7-, and 1,12-$C_2B_{10}H_{12}$ cages leads to 7,8-, 7,9-, and 2,9-*nido* 11-vertex cages, respectively. The [*nido*-7,8-$C_2B_9H_{12}$] ; features a five-membered C_2B_3 open face having a perpendicular plane of symmetry passing between the two adjacent carbon atoms and through the unique boron atom of the open face. The unique boron atom of the cage face possesses two hydrogen atoms in *exo*, extending away from the open cage face, and *endo*, lying over the open cage face, positions (117). Deprotonation of the *endo* hydrogen of [*nido*-$C_2B_9H_{12}$] ; leads to the [*nido*-$C_2B_9H_{11}$]^{2} ; dianion. Protonation of the [*nido*-7,8-$C_2B_9H_{12}$] ; anion with strong acids leads to the neutral highly acidic $C_2B_9H_{13}$ molecule.

Aside from their extensive use in metallacarborane chemistry, the dicarbollide anions are important intermediates in the synthesis of other carborane compounds. For example, aqueous ferric chloride oxidation of the [7,8-$C_2B_9H_{11}$] ; anion results in the 10-vertex cage *nido*-5,6-$C_2B_8H_{12}$ (118) and the aqueous chromic acid oxidation of [7,9-$C_2B_9H_{11}$] ; yields *arachno*-1,3-$C_2B_7H_{13}$ *[17653-38-2]* (29).

Nonicosahedral carboranes can be prepared from the icosahedral species by similar degradation procedures or by reactions between boranes such as B_4H_{10} and B_5H_9 with acetylenes. The degradative reactions for intermediate $C_2B_nH_{n+2}$ species ($n = 6-9$) have been described in detail (119). The small *closo*-$C_2B_nH_{n+2}$ species ($n = 3-5$ are obtained by the direct thermal reaction (500–600°C) of B_5H_9 using acetylene in a continuous-flow system. The combined yields approach 70% and the product distribution is around 5:5:1 of 2,4-$C_2B_5H_7$ *[20693-69-0]* to 1,6-$C_2B_4H_8$ *[20693-67-8]* to 1,5-$C_2B_3H_5$ *[20693-66-7]* (120). A similar reaction (eq. 60) employing base catalysts, such as 2,6-dimethylpyridine, at ambient temperature gives *nido*-2,3-$C_2B_4H_8$ *[21445-77-2]* (121). The [*nido*-$C_2B_4H_7$] ; anion can be prepared by deprotonation of *closo*-$C_2B_4H_8$.

$$B_5H_9 + HC{\equiv}CH \rightarrow 2,3\text{-}C_2B_4H_8 + L{\cdot}BH_3 \quad (L = \text{base}) \tag{60}$$

The *arachno* carboranes 1,3-$C_2B_7H_{13}$ (29) and 6,9-$C_2B_8H_{14}$ *[38670-58-5]* (122) are unusual in that two of the extra hydrogens occur in CH_2 groups. The other two extra hydrogens are present as B–H–B bridges. The compound *arachno*-CB_8H_{14} contains one CH_2 group and four bridging hydrogens. The CH_2 groups in these *arachno* carboranes are quite acidic and can be deprotonated readily to give the corresponding carborane mono- and dianions, which are useful synthetic reagents. Deprotonation at carbon has been demonstrated by deuterium exchange experiments.

As with the simple boranes, the *closo* carboranes are generally more thermally stable than the corresponding *nido* and *arachno* species. Thermal decomposition of *nido* and *arachno* carboranes often leads to one or more *closo* carborane. For example, pyrolysis of 2,3-$C_2B_4H_8$ is another route to 2,3-$C_2B_5H_7$ *[30347-95-6]*, 1,2-$C_2B_4H_8$ *[20693-68-9]* and 1,6-$C_2B_4H_8$ *[20693-67-8]*, and 1,5-$C_2B_3H_5$ *[20693-66-7]* (123).

A readily accessible carborane is *nido*-7-(NH_3)-7-$CB_{10}H_{12}$ *[12539-44-5]*, a zwitterionic species formally derived from [$CB_{10}H_{13}$] ; by replacement of a H by NH_3. It has been shown (124) that this monocarbaborane can be obtained in excellent yield by treatment of $B_{10}H_{14}$ with CN^- ; followed by passage through an acidic ion-exchange column (eq. 61).

$$B_{10}H_{14} + 2\,NaCN \xrightarrow[HCN]{H_2O} Na_2[B_{10}H_{13}CN] \xrightarrow{H^+} CB_{10}H_{12}(NH_3) \tag{61}$$

The related mono-*N*-alkylated carboranes, 7-(NH_2R)-7-$CB_{10}H_{12}$, can be prepared by treatment of decaborane(14) with alkyl isocyanides (125).

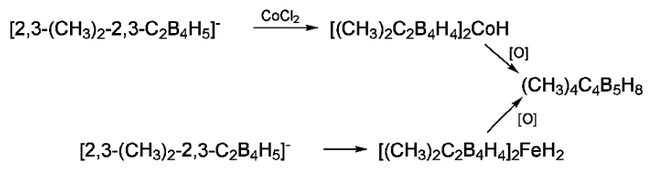
$$B_{10}H_{14} + RCN \rightarrow CB_{10}H_{12}(NH_2R) \tag{62}$$

The nitrogen of these aminocarboranes can be alkylated to give, eg, 7-[$N(CH_3)_3$]-7-$CB_{10}H_{12}$ *[31117-16-5]*. These compounds give [*closo*-2-$CB_{10}H_{11}$] ; *[38102-45-0]* upon treatment with Na in tetrahydrofuran (THF) followed by iodine oxidation (eq. 63) (126).

$$[CB_{10}H_{12}(NR_3)] \xrightarrow[THF]{Na} [CB_{10}H_{11}]^{3-} + NR_3 + 1/2\,H_2 \xrightarrow{I_2} [CB_{10}H_{11}]^- + 2\,I^- \tag{63}$$

Other large monocarbaboranes include *nido*-6-(NR_3)-6-CB_9H_{11} [*closo*-1-CB_9H_{10}] ; *[38192-43-7]* and [*closo*-$CB_{11}H_{12}$] ; *[39102-46-0]*. The *closo* monocarbaboranes can be functionalized at carbon via lithiation using reagents such as *n*-butyl lithium in a manner similar to the dicarbaboranes. The small monocarbaboranes *closo*-1-CB_5H_7 *[25301-90-0]*, *nido*-2-CB_5H_9 *[12385-35-2]*, and a variety of their alkylated derivatives are also known (127,128).

Tetracarbaboranes, which contain four carbon atoms in a single polyhedral skeleton, were rare until the discovery (129) of the metallacarborane-mediated synthesis of $(CH_3)_4C_4B_8H_8$ *[58815-26-2]*.



(64)

As the $C_4B_{n-4}H_n$ series of tetracarbaboranes is classified in the electron-counting formalism as *nido*, these molecules are expected to have open structures even though extra hydrogens are absent. Spectroscopic studies (130) have confirmed this expectation for 2,3,4,5-$C_4B_2H_8$ *[28323-17-3]*. One isomer of $(CH_3)_4C_4B_8H_8$ has the open nonicosahedral structure shown in Figure 11 and another isomer, the 1,2,3,8-tetramethyl compound *[54387-54-1]*, is apparently even more open (131). Other tetracarbaboranes include isomers of *nido*-$C_4B_8H_{10}$ and *nido*-$C_4B_7H_{11}$ (132).

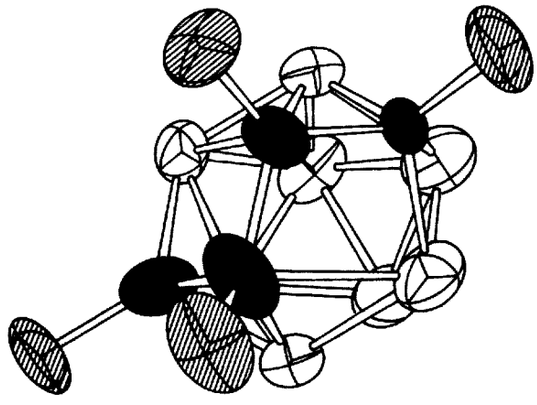


Fig. 11. Structure of $(CH_3)_4C_4B_8H_8$ with hydrogen atoms omitted. ○, BH; ⊘, CH_3; ●, C.

Courtesy of the American Chemical Society (131).

Cage rearrangements in polyhedral carboranes have been studied. Although most carborane cages are stable at room temperature, they frequently undergo rearrangements at elevated temperatures. Many of the carborane isomers obtained by conventional synthetic routes are kinetic products and not the thermodynamically most stable isomers. When subjected to elevated temperatures below the ultimate decomposition temperatures, carboranes often undergo rearrangements to the more stable isomers. This process may involve the sequential formation of a series of successively more stable isomers. Isomerization of the *closo*-1,2-$C_2B_{n-2}H_n$ ($5 \leq n \leq 12$) carboranes and their *C*-substituted derivatives has attracted considerable interest. Perhaps most intensely studied is the rearrangement of *closo*-$C_2B_{10}H_{12}$ (see Fig. 10). This rearrangement reflects a progression toward greater stability as a result of increasing carbon atom separation within the cage. The mechanisms for this cage rearrangement, as well as the rearrangements of other carboranes, heterocarboranes, and metallacarboranes, has been a topic of much controversy (133). A number of mechanisms have been proposed including most notably the diamond–square–diamond, modified diamond–square–diamond, triangular face rotation, pentagonal rotation, and opening closure processes, among others. In addition to thermal cage rearrangements, a number of carborane species are believed to undergo reversible rearrangements in solution at or near room temperature. For example, ^{11}B nmr spectral data indicates that the $[CB_{10}H_{11}]^-$ ion (134) and *closo*-C_2BH_8 (135) may be fluxional in solution.

A diversity of polyhedral carborane cage-containing polymers has been prepared. The best known of these are elastomeric polycarboranylsiloxanes which where developed by Olin Corp. (136) and Union Carbide Corp. (137). These are based on *m*-carborane cages linked by polysiloxane groups with direct C–Si bonds. The properties of these materials can be varied by changing the length and substituents of the polysiloxane linkages as well as their overall molecular weights. Some of these materials have excellent thermal stabilities, chemical resistance, and high temperature elastomeric properties. Polymers of this type, known under the trade name Dexsil, are commercial materials, useful as stationary phases in gas chromatography among other applications. The organic and organometallic chemistry of *closo* carborane derivatives has been reviewed (5,138).

Other Heteroboranes. Other well-documented families of heteroboranes include the azaboranes, phosphaboranes, arsenaboranes, stibaboranes, selenaboranes, and telluraboranes. Table 5 lists representative examples of heteroboranes from Groups 15 (V) and 16 (VI). The thiaboranes are the most extensively developed class of heteroboranes after the carboranes. The thiaboranes [*arachno*-6-SB_9H_{12}]$^-$ *[45979-10-0]* and *nido*-6-SB_9H_{11} *[59120-72-8]* (145) can be converted (eq. 65) to 1-SB_9H_9 *[41646-56-4]*, which has a nonicosahedral fragment structure (22).

$$B_{10}H_{14} \xrightarrow[H_2O]{S_8^2-} [arachno\text{-}6\text{-}SB_9H_{12}]^- \xrightarrow[C_6H_6]{I_2} nido\text{-}6\text{-}SB_9H_{11} \xrightarrow{\Delta} closo\text{-}1\text{-}SB_9H_9 \tag{65}$$

Preparation of the smaller thiaboranes, 4-SB_8H_{10}, occurs via

$$closo\text{-}1\text{-}SB_9H_9 \xrightarrow[CH_3OH]{KOH} [4\text{-}SB_8H_9]^- \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} 4\text{-}SB_8H_{10} \tag{66}$$

The thiaboranes [*arachno*-6-SB_9H_{12}]$^-$ and larger species are attainable by expansion reactions.

$$[6\text{-}SB_9H_{12}]^- \xrightarrow{\Delta, H^+} 7\text{-}SB_{10}H_{12} \xrightarrow{R_3NBH_3} SB_{11}H_{11} \tag{67}$$

Closo-1-SB_9H_9 and *closo*-$SB_{11}H_{11}$, unlike most other thiaboranes, are resistant to moisture and air oxidation. Other thiaboranes include the nine-vertex clusters *arachno*-$S_2B_7H_9$ (147) and *arachno*-SB_8H_9 (22), which are isostructural with *arachno*-$C_2B_7H_{13}$. These can be prepared in high yield.

Table 5. Heteroboranes

Heteroborane[a]	CAS Registry Number	References
Group 15 (V) Heteroatoms		
arachno-6-NB_8H_{13}	*[58920-21-1]*	139
nido-10-C H_5CH_2-7,8,10-$C_2NB_8H_{10}$	*[58614-34-9]*	139
nido-7-CH_3-7-$PB_{10}H_{12}$	*[57108-87-9]*	140
closo-C $H_5PB_{11}H_{11}$	*[57139-68-1]*	141
closo-1,7-$CPB_{10}H_{11}$	*[17398-92-4]*	141
[*nido*-7,8-CPB_9H_{11}]	*[52110-38-0]*	24
closo-1,2-$As_2B_{10}H_{10}$	*[51292-90-1]*	142
[*nido*-7-$AsB_{10}H_{12}$]	*[51292-97-8]*	142
[*nido*-7,8-$As_2B_9H_{10}$]	*[51358-26-0]*	143
[*closo*-$AsB_{11}H_{11}$]	*[51898-88-5]*	142
closo-1,2-$CAsB_{10}H_{11}$	*[23231-66-5]*	144
Group 16 (VI) Heteroatoms		
closo-$SB_{11}H_{11}$	*[56464-75-6]*	22
[*arachno*-6-SB_9H_{12}]	*[51358-27-1]*	145

nido-4-SB_8H_{10}	*[59351-07-4]*	22
closo-1-SB_9H_9	*[41646-56-4]*	22
nido-7-$SB_{10}H_{12}$	*[58984-44-4]*	146
arachno-6,8-$S_2B_7H_9$	*[63115-77-5]*	147
arachno-6,8-CSB_7H_{11}	*[63115-78-6]*	147
nido-7-$SeB_{10}H_{12}$	*[61649-90-9]*	148
nido-7,8-$Se_2B_9H_9$	*[61618-06-2]*	148
nido-7-$TeB_{10}H_{12}$	*[61649-91-0]*	148

[a] The *closo, nido, arachno* classification is given on the basis of framework electron count and not structure.

Metallaboranes

Transition-Element Metallaboranes. The transition-metal hydroborate cluster, $HMn_3(CO)_{10}(BH_3)_2$, containing a B_2H moiety, which is multiply bridging between three manganese carbonyl and manganese carbonyl hydride centers via M–H–B bridges, might be regarded as the first structurally characterized metallaborane cluster (149). This and similar clusters were isolated in the 1960s as by-products in the synthesis of transition-metal carbonyl hydrides by sodium borohydride reduction of metal carbonyls, a standard method for the preparation of transition-metal hydride complexes and clusters since the 1970s (150). The chemistry of stable metallaboranes which incorporate metals in vertex positions of polyhedral borane clusters was developed somewhat later. By 1990 a great many *nido* metallaborane clusters had been characterized covering a wide range of sizes and polyhedral fragment geometries.

One of the most extensive classes of metallaboranes are those derived from decaborane, which in most cases produces 11-vertex metallaborane products. The $[B_{10}H_{12}]^{2-}$ *[12430-37-4]* anion can also be considered as a bidentate ligand which coordinates metals between boron atoms 2,11 and 3,8, the metal at position 7 (Fig. 1**n**) such that the metal in effect occupies the position of a bridge hydrogen of the conjugate acid borane. Situations in which a metal vertex may be regarded as equivalent to an H^+, BH^{2+}, or the BH_2^+ moiety have also been discussed (151,152). In the case of the $[B_{10}H_{12}]^{2-}$ ligand, the bridge hydrogens lie in positions 8,9 and 10,11. Typical complexes containing $[B_{10}H_{12}]^{2-}$ include: $[M(B_{10}H_{12})_2]^{2-}$ where M = Zn, Cd, Hg (153), Co, Ni, Pd, Pt (154); $L_2M(B_{10}H_{12})$ where M = Pd, Pt; L = PR_3 (154); and $[L_3M(B_{10}H_{12})]^-$ where M = Co, Rh, Ir; L = CO, PR_3 (154). The x-ray structure of $[Ni(B_{10}H_{12})_2]^{2-}$ *[31388-28-0]* is shown in Figure 12 (155). If the $[B_{10}H_{12}]^{2-}$ ligand in the Ni complex is considered to be bidentate, coordination about the metal is effectively square planar. The geometry of the metal in analogous complexes varies according to the requirements of the metal. For example, $[Zn(B_{10}H_{12})_2]^{2-}$ *[19154-53-1]* is tetrahedral (156). The $[B_{10}H_{13}]^-$ ion *[36928-50-4]* (157) is especially useful for the synthesis of 11-vertex *nido* metallaboranes. These syntheses are influenced by (*1*) the cation of the $[B_{10}H_{13}]^-$ salt; (*2*) the nature of other ligands about the metal; and (*3*) the availability of a proton trap for the reaction (154,158).

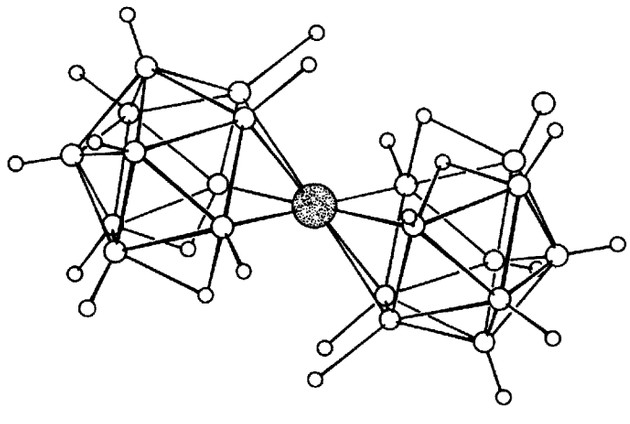


Fig. 12. The structure of $[Ni(B_{10}H_{12})]^{2-}$ (155) where ▩ represents the Ni; ○, B; and ○, H.

The first *closo* metallaborane complexes prepared (159) were the nickelaboranes $[closo\text{-}(\eta^5\text{-}C_5H_5)Ni(B_{11}H_{11})]^-$ and *closo*-1,2-$(\eta^5\text{-}C_5H_5)_2$-1,2-$Ni_2B_{10}H_{10}$ *[55266-88-1]* (Fig. 13). These species are equivalent to $[closo\text{-}CB_{11}H_{12}]^-$ and *closo*-$C_2B_{10}H_{12}$ by the electron-counting formalism. The mixed bimetallic anion $[closo\text{-}(\eta^5\text{-}C_5H_5)_2CoNi(B_{10}H_{10})]^-$ and other related species were reported later (160). These metallaboranes display remarkable hydrolytic, oxidative, and thermal stability.

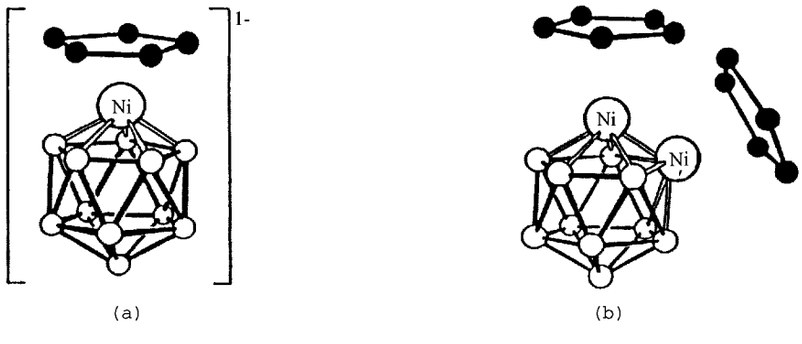


Fig. 13. The structures of *closo* metallaboranes where ○ represents BH; ●, CH: (**a**) $[closo\text{-}(\eta^5\text{-}C_5H_5)Ni(B_{11}H_{11})]^-$;; (**b**) *closo*-1,2-$(\eta^5\text{-}C_5H_5)_2$-1,2-$Ni_2B_{10}H_{10}$.

Closo metallaboranes can also be formed by the direct interaction of polyborane and metal carbonyl clusters. For example,

$$\textit{arachno}\text{-}B_{10}H_{12}[S(C_2H_5)_2]_2 + Co_2(CO)_8 \xrightarrow[120^\circ C]{\text{toluene}} \textit{closo}\text{-}(CO)_5Co_2B_{10}H_8[S(C_2H_5)_2]_2 + 3\,CO + 2\,H_2 \quad (68)$$

yields two isomers of this 12-vertex *closo* compound in good yield (161). Both isomers contain a $Co_2(CO)_8$ cobalt carbonyl cluster fragment, which can be considered a four framework electron-donor group. The retention of two $S(C_2H_5)_2$ substituents allows these clusters to comply with electron-counting rules for a *closo* compound. The B–SR_2 groups are three framework electron-donor groups. The structure of one isomer of *closo*-$(CO)_5Co_2B_{10}H_8[S(C_2H_5)_2]_2$ is shown in Figure 14.

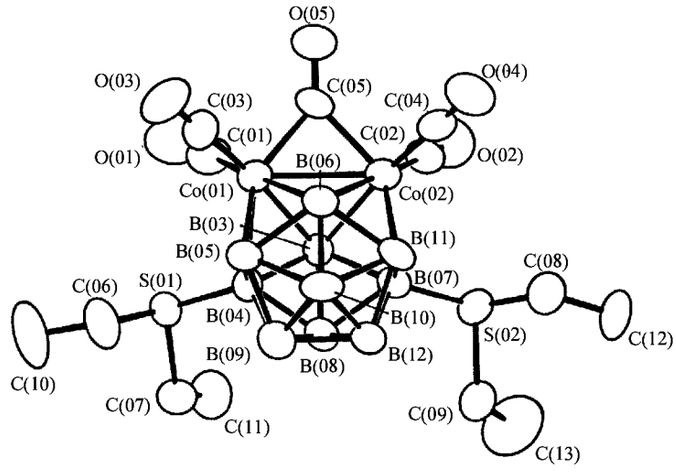


Fig. 14. The structure of one isomer of *closo*-$(CO)_5Co_2B_{10}H_8[S(C_2H_5)_2]_2$ without the hydrogens.

Courtesy of the American Chemical Society (161).

A number of novel products have been isolated from the reaction of $[B_5H_8]^-$ *[31426-87-6]* and $CoCl_2$ and $[C_5H_5]^-$ in THF (162,163). The predominant product is *nido*-2-(CpCo)-B_4H_8 *[43061-99-0]*. Also obtained are isomeric clusters containing up to four cobalt atoms, eg, $(\eta^5\text{-}C_5H_5Co)_4B_4H_8$ *[59370-82-0]*. Characterization of these clusters indicate an unusual 2*n* framework electron count having geometries reminiscent of strictly metallic clusters (11,164).

Main Group Element Metallaboranes. A variety of metallaborane clusters, which incorporate main group metals in vertex positions of polyhedral metallaborane clusters, have been reported. Examples are $(BH_4)BeB_5H_{10}$ (165), $MgB_{10}H_{12}\cdot 2O(C_2H_5)_2$ (166), $[(CH_3)HgB_{10}H_{12}]^-$ (167), $[AlB_{10}H_{14}\cdot 2O(C_2H_5)_2]^-$ (168), $[(CH_3)AlB_{11}H_{11}]^2-$ (169), $(CH_3)InB_{10}H_{12}$ (167), $[(CH_3)_2TlB_{10}H_{12}]^-$ (167), and $(CH_3)_2MB_{10}H_{12}$ where M Si (170), Ge (171), or Sn (171). A number of main group metal complexes have been reported which incorporate borane moieties via M–H–B bridges, such as those found in $Al(BH_4)_3$ (Fig. 8). Examples of other compounds in this class include the octahydrotriborate complexes $Be(B_3H_8)_2$ (172), $(C_5H_5)BeB_3H_8$ (172), $[(CH_3)BeB_3H_8]_2$ (172), $(CH_3)_2AlB_3H_8$ (173), $H_2GaB_3H_8$ (174), $(CH_3)_2GaB_3H_8$ (174), $Mg(B_3H_8)_2\cdot 6THF$ (175), and $(BH_4)MgB_3H_8\cdot 5THF$ (175), THF tetrahydrofuran. Complexes containing the $[B_3H_8]^-$ unit are generally fluxional in solution. The low temperature static structure of $Be(B_3H_8)_2$ exhibits C_{2v} symmetry and features a tetrahedral beryllium center covalently linked via four Be–H–B bonds to two B_3H_8 units (176). The nmr spectral data for $[(CH_3)Be(B_3H_8)]_2$ indicates a methyl bridged dimer structure.

Several complexes containing the $B_5H_{10}Be$ unit, such as $(BH_4)BeB_5H_{10}$ and $Be(B_5H_{10})_2$ (165) have been characterized. X-ray diffraction studies (177) of these compounds show pentagonal pyramid structures having the beryllium atom in a basal position with three of the five bridging hydrogen atoms at the open face taking part in Be–H–B bonds. In $(BH_4)BeB_5H_{10}$, the BH_4 moiety is linked to the beryllium center by two Be–H–B bonds. The structure of $Be(B_5H_{10})_2$ consists of two pyramidal $B_5H_{10}Be$ units linked at a common basal position beryllium atom.

The volatile, air-sensitive liquid species $(CH_3)_2AlB_3H_8$ and $(CH_3)_2GaB_3H_8$ are prepared by the direct reaction of the corresponding main group metal halide and salts of the $[B_3H_8]^-$ ion, in the absence of solvent (178). The reaction of $(CH_3)_2AlB_3H_8$ and $Al(BH_4)_3$ results in the species $(BH_4)_2AlB_3H_8$. These small metallaboranes are fluxional in solution and have limited thermal stability at room temperature.

The high yield preparation of the *closo*-aluminaborane anion $[(CH_3)AlB_{11}H_{11}]^2-$ has been described (169).

$$Na_2[B_{11}H_{13}] + Al(CH_3)_3 \xrightarrow[110^\circ C,\ 4d]{\text{glyme (1 equiv.)}} Na_2[(CH_3)AlB_{11}H_{11}] + 2\,CH_4 \quad >90\% \quad (69)$$

Similar synthetic strategies involving the elimination of alkyl groups from organometallic reagents and acidic B–H–B groups have been used to prepare a number of other metallaboranes and metallacarboranes. The $[(CH_3)AlB_{11}H_{11}]^2-$ anion is isostructural with *closo*-$[B_{12}H_{12}]^2-$. The methyl group is attached to aluminum projecting radially from the icosahedral AlB_{11} cage.

The silacarborane analogue of C,C-dimethyl-*ortho*-carborane, *closo*-1,2-$(CH_3)_2$-1,2-$Si_2B_9H_{11}$ *[128270-48-4]* has been reported (179). This *o*-silacarborane, which has an icosahedral framework much like *o*-carborane and is reported to be stable to air and moisture, was obtained in low yield from the reaction of decaborane and bis(dimethylamino)methylsilane in refluxing benzene.

$$B_{10}H_4 + CH_3(H)Si[N(CH_3)_2]_2 \rightarrow \textit{closo}\ 1,2\ (CH_3)_2\ 1,2\ Si_2B_9H_{11} + 6,9\ [(CH_3)_2NH]_2B_{10}H_{12} + \text{other products} \quad (70)$$

Exopolyhedral Metallaboranes. Polyboranes may bind exopolyhedral metals in a variety of ways. Most commonly metals are bound via M–H–B interactions. In other cases metals may formally replace bridging hydrogen atoms at edge positions to give B–M–B interactions. Metals may also be attached to polyborane cages by direct M–B σ-bonds. M–H–B bonds are found in $Cu[B_{10}H_{10}]^-$ (180) and in $[[(C_6H_5)_3P]_2Cu]_2\text{-}\mu\text{-}B_{10}H_{10}$ *[54020-26-7]* (152). In both cases, the metal centers are bound through a bidentate interaction with two adjacent B–H groups.

A series of divalent lanthanide metal metallaborane derivatives have been prepared by the redox reaction of metallic lanthanides and boron hydrides and by the metathesis reaction of boron hydride salts with $LnCl_2$ where Ln Sm, Eu, Yb (181,182). The species $(CH_3CN)\ Yb[(\mu\text{-}H)_2B_{10}H_{12}]^-$,

$(CH_3CN)_4Yb[(\mu\text{-}H)_3BH]_2$, and $(C_5H_5N)_4Yb[(\mu\text{-}H)_3BH_4]_2$ have been structurally characterized by x-ray crystallography and shown to contain ytterbium to boron hydride Yb–H–B linkages. Thermal decomposition of lanthanaboranes can be used to generate lanthanide metal borides.

Metallaboranes containing M–B σ-bonds can be prepared by nucleophilic displacement reactions (183) and oxidative addition (184) of B–H and B–Br bonds to metal centers. For example, the reaction of $IrCl(CO)[P(CH_3)_3]_2$ and 1- or 2-BrB_5H_8 results in 2-$[IrBr_2(CO)\text{-}[P(CH_3)_3]_2B_5H_8]$ in which the B_5H_8 polyhedron serves as ligand for the metal.

Boranes also form derivatives in which main group elements occupy a bridging position between two boron atoms, rather than a polyhedral vertex. An extensively studied system is $\mu\text{-}R_3MB_5H_8$, where R H, CH_3, C_2H_5, halogen, and M Si, Ge, Sn, Pb (185). The structure of 1-Br-μ-$[(CH_3)_3Si]$-B_5H_7 *[28323-19-5]* is shown in Figure 15 (186).

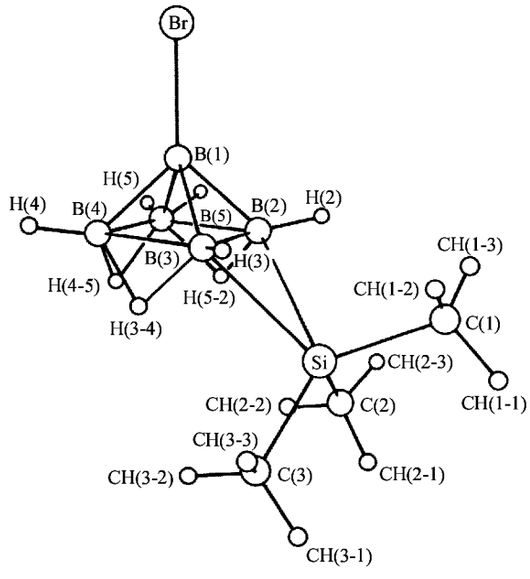


Fig. 15. Structure of 1-Br-μ-$[(CH_3)_3Si]B_5H_7$.

Courtesy of the American Chemical Society (186).

Metallacarboranes

In the early 1960s it was recognized (6,187) that there were bonding similarities between the pentagonal face of the isomeric $[nido\text{-}C_2B_9H_{11}]^{2-}$ ions and the well-known cyclopentadienide ion (Cp) $[C_5H_5]^-$ (Fig. 16). The isomeric $[nido\text{-}C_2B_9H_{11}]^{2-}$ ions, which are commonly known as dicarbollide ions, and many other carborane anions, form stable complexes with most of the metallic elements. Indeed nearly all metals can be combined with polyborane hydride clusters to produce an apparently limitless variety of cluster compounds.

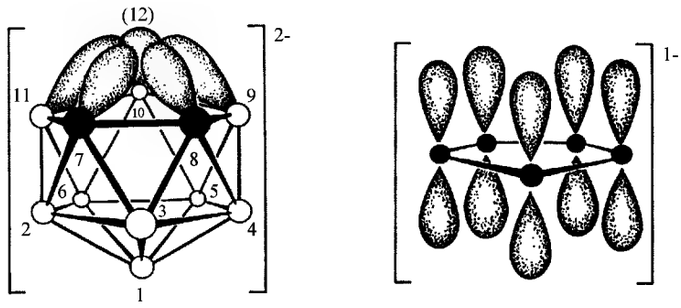


Fig. 16. Structural analogy between the $[7,8\text{-}C_2B_9H_{11}]^{2-}$ dicarbollide dianion and the $[C_5H_5]^-$ cyclopentadienide anion (6) where ○ represents BH; ●, CH; showing *p* orbital lobes.

Transition-Metal Metallacarboranes. The first demonstration of the insertion of a transition metal into an open face of a borane cage was with the iron sandwich compound $[common\text{-}Fe(C_2B_9H_{11})_{12}]^{2-}$ *[12541-50-3]* (188). This product is readily air-oxidized to $[common\text{-}(C_2B_9H_{11})_2Fe]^-$ *[12547-76-1]*, a complex containing a formal Fe^{3+} center. These complexes, as well as those formed from a variety of formally d^8, d^7, d^6, and d^5 transition metals (Table 6), have symmetrical sandwich structures (189) of the type shown in Figure 17**a**. By contrast, d^8 and d^9 metals form slipped sandwich structures as shown in Figure 17**b** (6,190). Transition metals have been incorporated into a myriad of icosahedral complexes based on the dicarbollide cage (190,191). Examples are

$$[nido\text{-}C_2B_9H_{11}]^{2-} + [C_5H_5]^- + M^{2+} \longrightarrow [closo\text{-}(\eta^5\text{-}C_5H_5)MC_2B_9H_{11}]^- \quad (71)$$

$$[closo\text{-}(\eta^5\text{-}C_5H_5)MC_2B_9H_{11}]^- \xrightarrow{[O]} closo\text{-}(\eta^5\text{-}C_5H_5)MC_2B_9H_{11}$$

where M Fe, Co, Ni, Cr.

Table 6. Structure of $[(C_2B_9H_{11})_2M^{n+}]^{n-4}$ Complexes as a Function of Electronic Configuration

Electronic configuration

d^5	d^6	d^7	d^8	d^9	d^{10}
		Unslipped sandwich[a]			
Cr^{3+}	Fe^{3+}	Fe^{2+} Co^{2+} Ni^{4+} Pd^{2+}	Co^{2+} Ni^{3+} Pd^{3+}		
		Slipped sandwich[b]			
				Cu^{3+} Ni^{2+} Pd^{2+} Au^{3+}	Cu^{2+} Au^{2+}

[a] See Figure 17**a**.

[b] See Figure 17**b**.

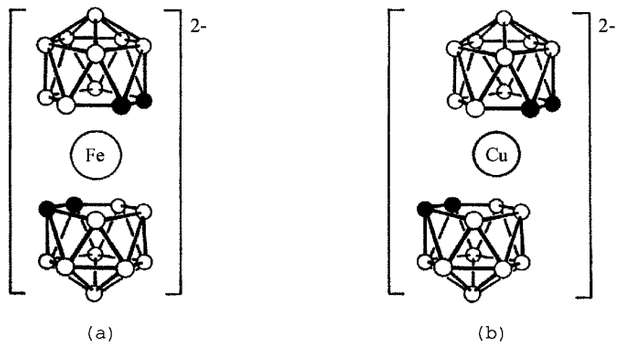


Fig. 17. Exemplary structures of (**a**) unslipped and (**b**) slipped metallacarborane dicarbollide sandwich derivatives where ○ represents BH; ●, CH.

Metallacarborane dicarbollide complexes are generally more robust than the corresponding cyclopentadiene complexes. The bis-dicarbollide sandwich complexes of general formula $[M(C_2B_9H_{11})_2]^-$, where M is Fe^{3+}, Co^{3+}, and Ni^{3+}, exhibit great thermal, chemical, redox, and radiolytic stability. These species are also unusual in that they are extremely hydrophobic anions which form very strong conjugate acids. This unique combination of features leads to a number of potential uses such as the extraction of organic compounds from extremely dilute solutions and the isolation of metal cations, including the quantitative separation of radionuclides, eg, ^{137}Cs (192).

Representative icosahedral metallacarborane carbonyl complexes are prepared as shown (193).

$$[nido\text{-}C_2B_9H_{11}]^{2-} + M(CO)_6 \xrightarrow[M\ =\ Cr,\ Mo,\ W]{h\nu} [closo\text{-}(C_2B_9H_{11})M(CO)_3]^- + 3\ CO \tag{72}$$

$$[nido\text{-}C_2B_9H_{11}]^{2-} + BrM(CO)_5 \xrightarrow[M\ =\ Mn,\ Re]{h\nu} [closo\text{-}(C_2B_9H_{11})M(CO)_3]^- + Br^- + 2\ CO \tag{73}$$

Fundamental methodologies for the synthesis and transformation of metallacarboranes (6) include polyhedral expansion (194–199), contraction (200), subrogation (201), and related reactions. Many carboranes are readily reduced from *closo* to *nido* molecules with a concomitant opening of the cage structures (see Fig. 2). The open, nontriangular faces of the resulting *nido* anions are generally capable of coordination to metals. The polyhedral expansion reaction (194–199), also called metal insertion, is most general for two carbon carboranes.

$$closo\text{-}C_2B_nH_{n+2} + 2e^- \rightarrow [nido\text{-}C_2B_nH_{n+2}]^{2-} \tag{74}$$

$$2\ nido\text{-}[C_2B_nH_{n+2}]^{2-} + M^{x+} \rightarrow [commo\text{-}M(C_2B_nH_{n+2})_2]^{x-4} \tag{75}$$

Multiple polyhedral expansion reactions, carried out either simuntaneously or sequentially, have been used to prepare metallacarboranes having multiple metal centers (202). An example is given in Figure 18.

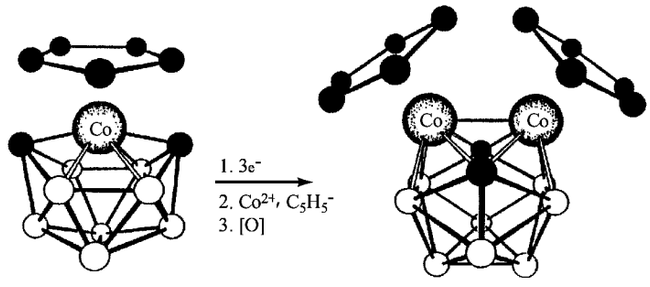


Fig. 18. Fig. 18. A characteristic polyhedral expansion reaction leading to isomeric $[(\eta^5\text{-}C_5H_5)Co]_2C_2B_8H_{10}$ clusters where ○ represents BH; ●, CH. The 2,9-$(\eta^5\text{-}C_5H_5)$-2,9-Co_2-1,12-$C_2B_8H_{10}$ isomer is shown.

Courtesy of the American Chemical Society (202).

In most cases the prolonged treatment of a *closo* carborane or borane with strong base results in the removal of a single-boron vertex to yield a *nido* cluster, inert to further degradation. This principle is exploited in the polyhedral contraction and subrogation synthetic strategies. In the prototypical case,

the polyhedral contraction reaction (200) involves the degradative removal of a formal $[BH]^{2+}$ vertex from a *closo n* vertex metallacarborane followed by a two-electron oxidation of the *nido* intermediate to produce the corresponding *closo n* 1 vertex metallacarborane. An example of the polyhedral contraction reaction is given in Figure 19 (200). Polyhedral subrogation (201) is similar to the polyhedral contraction except that instead of oxidation of the *nido* metallacarborane intermediate, this intermediate is trapped by insertion of a metal atom to provide a bimetallacarborane framework. In practice, this procedure often leads to polymetallacarboranes as shown in Figure 20 (202).

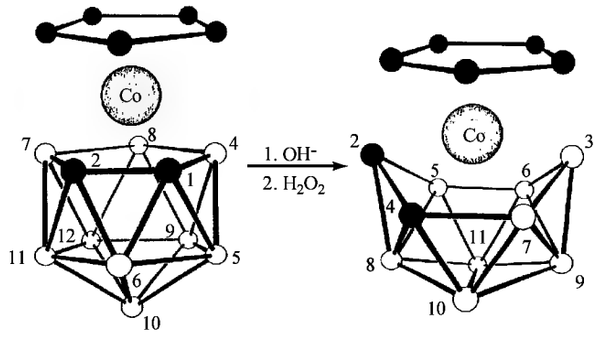


Fig. 19. A characteristic polyhedral contraction reaction leading to $(\eta^5\text{-}C_5H_5)CoC_2B_8H_{10}$ where ○ represents BH; ●, CH.

Courtesy of the American Chemical Society (200).

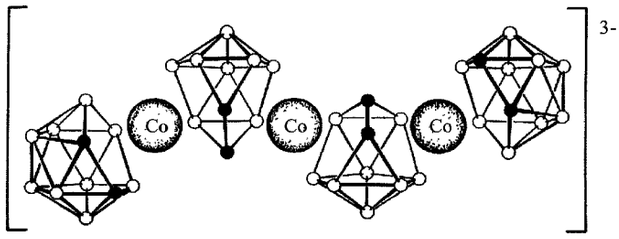


Fig. 20. A polymetallacarborane anion resulting from the polyhedral subrogation reaction where ○ represents BH; ●, CH.

Courtesy of the American Chemical Society (202).

Application of the polyhedral expansion methodology to $C_2B_{10}H_{12}$ leads to supraicosahedral metallacarboranes such as *closo*-$(\eta^5\text{-}C_5H_5)CoC_2B_{10}H_{12}$ *[33340-90-8]* (194–199). Further expansion of 13-vertex species or thermal metal transfer reactions leads to the 14-vertex cluster $[(\eta^5\text{-}C_5H_5)Co]_2C_2B_{10}H_{12}$ *[52649-56-6]* and *[52649-57-7]* (199). Similar 14-vertex species have been obtained from tetracarbaboranes (203) and show unusual structures. The isomeric bimetallic cobaltacarborane complexes *closo*-$(\eta^5\text{-CpCo})_2C_2B_8H_{10}$ (cp C_5H_5) can be formed by either polyhedral expansion or contraction reactions. Six isomers of this cluster are formed in the thermally-induced intermolecular metal transfer and polyhedral expansion of the 11-vertex *closo*-$(\eta^5\text{-}C_5H_5)CoC_2B_8H_{10}$.

Metallacarboranes are subject to thermal rearrangement reactions similar to those of carboranes and heteroboranes (204–206). In a study of the *closo* metallacarboranes $(\eta^5\text{-}C_5H_5)CoC_2B_nH_{n+2}$, n 6–10 (205), it was concluded that the empirical rules governing thermal rearrangements are (*1*) the transition-metal atom preferentially occupies the highest order vertex; (*2*) the carbon atoms do not decrease their mutual separation; (*3*) carbon atoms migrate to the lowest order vertices; and (*4*) carbon atoms migrate away from the transition metal providing rules (*2*) and (*3*) are not violated. Exceptions have been found, but at least some exceptions result from kinetic rather than thermodynamic control of the rearrangement (203).

A good example of the relationship between metallacarborane structure and the electronics of the metal center is found in the "pinwheel cluster" shown in Figure 21 (207). In this trimeric cupracarborane three *nido* dicarbollide ligands, each charge compensated by substitution of an H: by methyl nicotinate, are η^3-bonded to a Cu^+ ion and to a neighboring copper center via B–H–Cu bonds. This cluster, which has crystallographic C_3 symmetry and three equal Cu–Cu bond distances, is stabilized by M–H–B bonding in much the same way that metal carbonyl clusters are stabilized by bridging CO groups.

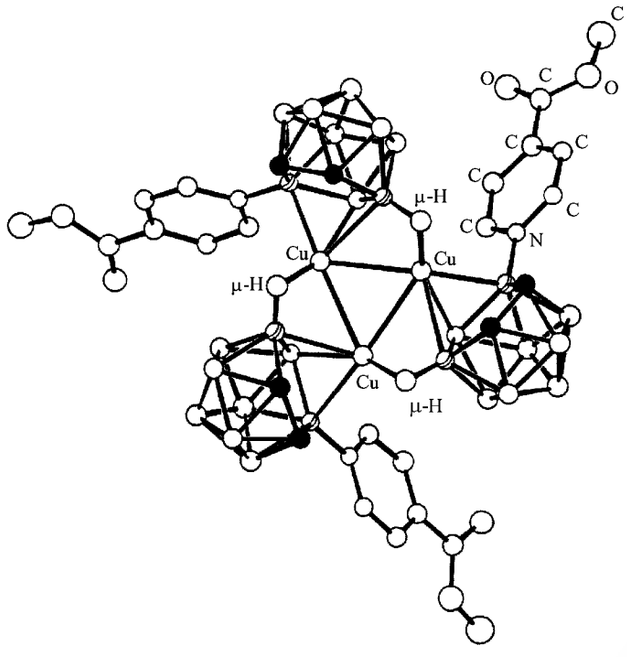


Fig. 21. Molecular structure of the metallacarborane pinwheel cupracarborane complex $[Cu_3(\mu\text{-}H)_3\{C_2B_9H_9(4\text{-}(C_5H_4N)COOCH_3)\}_3]$ where within the cage structure ◑ represents B; ○, BH; and ●, carboranyl CH.

Courtesy of the American Chemical Society (207).

Metallacarboranes containing early transition metals including Ti, V, Cr, Mn, Zr, and Hf in a variety of oxidation states are especially unique (208). For example, the titanium 2+, 3+, and 4+ compounds $[commo\text{-}Ti(C_2B_{10}H_{12})_2]^{2-}$; *closo*-$(\eta^5\text{-}C_5H_5)TiC_2B_{10}H_{12}$, *closo*-$(C_8H_8)TiC_2B_{10}H_{12}$, and *closo*-$(C_8H_8)TiC_2B_9H_{11}$ have no counterparts in traditional organometallic chemistry (209). These compounds exhibit remarkable thermal stability.

A precursor to several *closo* 10-vertex cobaltacarboranes is *arachno*-$[C_2B_7H_{11}]^{2-}$; *[42319-46-0]*, which is obtained by the deprotonation of 6,8-$C_2B_7H_{13}$ *[17653-38-2]*. When treated with excess $CoCl_2$ and cyclopentadienide ion *[12127-83-2]*, $[C_2B_7H_{11}]^{2-}$; gives *closo*-$(\eta^5\text{-}C_5H_5)Co(C_2B_7H_9)$ *[37381-23-0]* and *[51539-00-5]* (eq. 76) which occurs as two isomers, *closo*-2-$[(\eta^5\text{-}C_5H_5)Co]$-1,6-$C_2B_7H_9$ *[41348-11-2]* and *closo*-2-$[(\eta^5\text{-}C_5H_5)Co]$-1,10-$C_2B_7H_9$ *[42808-86-6]* (29).

$$[C_2B_7H_{11}]^{2-} + [C_5H_5]^- + \frac{3}{2}Co^{2+} \rightarrow H_2 + \frac{1}{2}Co + (C_5H_5)Co(C_2B_7H_9) \tag{76}$$

An interesting *closo* 10-vertex monocarbon metallacarborane species is *closo*-10-$[(C_5H_5)Ni]$-1-CB_8H_9 *[52540-76-8]* (210) which contains a metal atom bound to a B_4-face. *Nido* 10-vertex metallaboranes frequently have boatlike frameworks where the metal is at the 6- or 9-position; however, the nature of the bonding depends on the metal. Examples of nine-vertex metallacarboranes include $[closo\text{-}2\text{-}(CO)_3\text{-}2,1,6\text{-}MnC_2B_6H_8]^-$; *[41267-49-6]* (211), which has the expected tricapped trigonal prism structure, and the clusters $[(C_5H_5)Ni]_2C_2B_5H_7$ *[51108-05-5]* (212) and 6,8-$(CH_3)_2$-1,1-$[P(CH_3)_3]_2$-1,6,8-$PtC_2B_6H_8$ (213).

Many structures are possible for the smaller metallacarboranes and various synthetic strategies are available. Especially noteworthy is the occurrence of triple- and tetradecker sandwich compounds (214). The polyhedral expansion synthetic strategy can also be used with small carboranes (212). For instance, the small metallacarborane *closo*-1,1,1-$(CO)_3$-1,2,3-$FeC_2B_4H_6$ *[32761-40-3]* (212) is obtained from $C_2B_4H_8$ upon treatment with $Fe(CO)_5$.

Exopolyhedral Metallacarboranes. Many metallacarboranes are known that exhibit exopolyhedral bonding to metals. Most commonly metals are bound via M–H–B interactions in which the B–H group can be regarded as a two-electron donor to the metal center. In other cases, M–B, M–C, or M–M bonding may be involved. For example, electron-rich transition-metal complexes are capable of activating carboranyl B–H bonds leading to B-metallated metallacarboranes. Thus the d^8 Ir^+ complex $[Ir(C_8H_{14})_2Cl]_2$ reacts with 1,2-, 1,7-, and 1,12-$C_2B_{10}H_{12}$ carboranes in the presence of triphenylphosphine to give regiospecific B-metallated oxidative addition products of the type $\{[(C_6H_5)_3P]_2IrHCl\}$-*closo*-$C_2B_{10}H_{11}$ (215,216). Similarly, the *C*-substituted phosphinacarborane 1-$[(CH_3)_3P]$-*closo*-$C_2B_{10}H_{11}$ reacts with $[Ir(C_8H_{14})_2Cl]_2$ to give a metallacycle containing an Ir–B bond (216,217). An example of exopolyhedral metal binding by a combination of M–M and M–H–B bonding is given in Figure 22. This complex is formed in the reaction of copper(I) chloride, $(C_6H_5)_3P$, and $[closo\text{-}3,1,2\text{-}TlC_2B_9H_{11}]^-$; (218). A variety of metallacarborane complexes containing metal–metal bonds between cage framework metal centers and exopolyhedral metal centers have also been prepared (219).

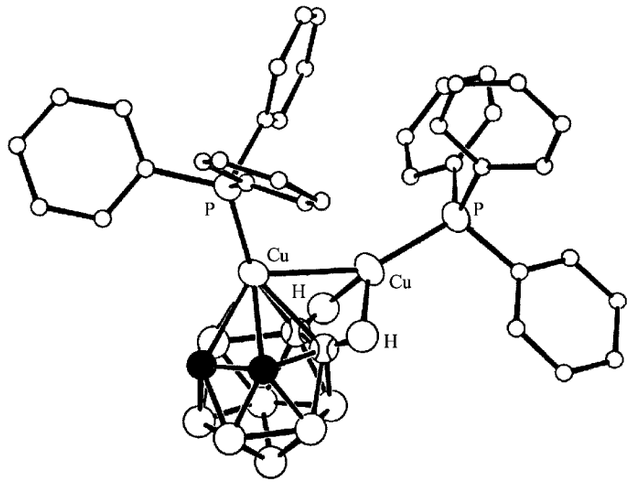


Fig. 22. The molecular structure of [*closo-exo*-4,8-{(μ-H)$_2$Cu[P(C H$_5$)$_3$]}-3-[(C H$_5$)$_3$P]-3,1,2-CuC$_2$B$_9$H$_9$ where within the cage structure ⓑ represents B; ^, BH; and ●, carboranyl CH.

Courtesy of the American Chemical Society (218).

Metallacarboranes in Catalysis. Perhaps the most intensely studied of all metallacarborane complexes is the exopolyhedral metallacarborane *closo*-3,3-[P(C H$_5$)$_3$]$_2$-3-H-3,1,2-RhC$_2$B$_9$H$_{11}$ *[61250-52-0]*, shown in Figure 23**a**, and its cage *C*-substituted derivatives. The three available isomers of *closo*-[P(C H$_5$)$_3$]$_2$(H)Rh-C$_2$B$_9$H$_{11}$ are synthesized in high yield by the oxidative addition of [P(C H$_5$)$_3$]$_2$RhCl with the appropriate [*nido*-C$_2$B$_9$H$_{12}$] ; ion (220), which may also be made chiral by the attachment of a single-alkyl or -aryl group at a carbon position (221). The resulting hydridorhodacarboranes are quite robust and catalyze a number of reactions including the isomerization and hydrogenation of olefins, the deuteration of B–H groups, and the hydrosilanolysis of alkenyl acetates. These species function as homogeneous catalyst precursors for the isomerization and hydrogenation of olefins as well as other reactions (222). Extensive investigations of rhodacarborane catalysts and the mechanisms responsible for their activity revealed the novel *closo–nido* tautomerism illustrated in Figure 23**a** and **b**. When alkyl or aryl substituents are present at the carborane carbon atoms, the usual rhodacarborane complex isolated is not the *closo* species, but rather an *exo–nido* complex in which the [P(C H$_5$)$_3$]$_3$Rh$^+$ center is bonded to the [*nido*-7,8-(R)$_2$-7,8-C$_2$B$_9$H$_{12}$] ;, (R alkyl, aryl), ions by a pair of Rh–H–B three-center, two-electron bridge bonds (223). The formation of *exo–nido* tautomers in this rhodacarborane system has been attributed primarily to steric factors. The isolation of *closo* structures for *C*-substituted isomers, which carry their substituent steric bulk removed from the metal center, such as *closo*-2,2-[P(C H$_5$)$_3$]-2-H-1-(CH$_3$)-7-(C H$_5$)-2,1,7-RhC$_2$B$_9$H$_{11}$, supports this contention.

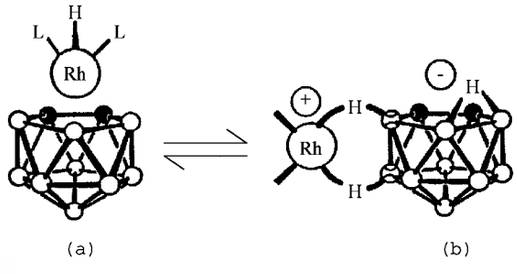


Fig. 23. (**a**) The structure of *closo*-3,3-[(C H$_5$)$_3$P]$_2$-3-H-3,1,2-RhC$_2$B$_9$H$_{11}$, and (**b**) one isomer of its tautomer *exo-nido*-(L$_2$Rh)$_2$-(μ-H)$_2$-7,8-C$_2$B$_9$H$_{12}$ where L is (C H$_5$)$_3$P. ⊖ represents B; ○, BH; ●, CH.

The generality of *closo–exo–nido* redox equibria in solution for these rhodacarborane species was demonstrated by labeling studies using derivatives of the *nido*-carborane precursor anion having a bridging B–D–B group. The deuterium is specifically transferred to the rhodium vertex of the *closo* tautomer (224). Retention of the D-label at the rhodium center during catalytic reactions proves that the H- (or D-) ligand attached to the [P(C H$_5$)$_3$]$_2$RhH vertex does not participate in the catalytic processes, but is sequestered in the B–D–B bridge of the catalytically active *exo–nido* tautomer or related structure. The contention that the rhodacarborane *exo–nido* tautomer is the actual catalyst in solution is further supported by the observation that the catalytic hydrogenation and isomerization of alkenes exhibits the same characteristics and reaction rate law regardless of whether these reactions are conducted using a *closo* species or one of its *exo–nido* counterparts (225). In addition, the occurrence of facile carborane cage exchange reactions coupled with rate data obtained for such processes also implicates a reactive *exo–nido* intermediate (226).

Rhodacarborane catalysts have been immobilized by attachment to polystyrene beads with appreciable retention of catalytic activity (227). A 13-vertex *closo*-hydridorhodacarborane has also been synthesized and demonstrated to possess catalytic activity similar to that of the icosahedral species (228). Air-oxidation of *closo*-3,3-[P(C H$_5$)$_3$]$_2$-3-H-3,1,2-RhC$_2$B$_9$H$_{11}$ results in a brilliant purple dimer. This compound contains two formal Rh^{2+} centers linked by a sigma bond and a pair of Rh–H–B bridge bonds. A number of similar dimer complexes have been characterized and the mechanism of dimer formation in these rhodacarborane clusters have been studied in detail (229).

The exopolyhedral metallacarborane complex Ti(C$_2$B$_{10}$H$_{11}$)$_4$, which is prepared by the reaction of TiCl$_4$ and 1-Li-1,2-C$_2$B$_{10}$H$_{11}$, has also been reported to be an active heterogeneous catalyst for the polymerization of olefins when supported on alumina and in the presence of (C$_2$H$_5$)$_2$AlCl co-catalyst (230).

Main Group Element Carborane Derivatives. Main group element carborane derivatives have been reviewed (231). Only a few alkaline-earth element metallacarborane derivatives have been characterized. The icosahedral beryllacarborane, *closo*-3-[(CH$_3$)$_3$N]-3,1,2-BeC$_2$B$_9$H$_{11}$, shown in Figure 24**a**, has been prepared via the reaction of *nido*-7,8-C$_2$B$_9$H$_{13}$ and Be(CH$_3$)$_2$ [O(C$_2$H$_5$)$_2$]$_2$ followed by reaction of the diethyletherate product and trimethylamine (234).

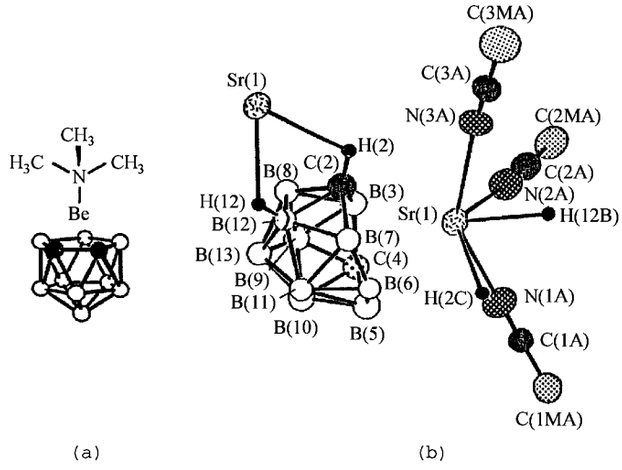


Fig. 24. (**a**) The proposed structure of *closo*-3-$(CH_3)_3N$-3,1,2-$BeC_2B_9H_{11}$ where ○ represents BH; ●, CH; and (**b**) the x-ray structure of the polymeric [*closo*-1,1,1-$(CH_3CN)_3$-1,2,4-$SrC_2B_{10}H_{12}]_n$ showing the metal to carborane interaction with the metal of the adjacent monomer unit. ⊕ represents B; ○, BH; ▨, C; ⊙, CH; ⊗, CH_3; ⊗, N; ⊙, Sr; and ●, H. A indicates an atom on the CH_3CN ligand; MA is the methyl group; H(12B) is the hydrogen bound to the boron at position 12; H(2C) is the hydrogen bound to the carbon at position 2.

Courtesy of the American Chemical Society (232,233).

The reaction of calcium iodide and strontium iodide and the [*nido*-$C_2B_{10}H_{12}]^{2-}$ ion in tetrahydrofuran (THF) followed by treatment with acetonitrile provides the metallacarboranes [*closo*-1,1,1,1-$(CH_3CN)_4$-1,2,4-$CaC_2B_{10}H_{12}$ (232) and [*closo*-1,1,1-$(CH_3CN)_3$-1,2,4-$SrC_2B_{10}H_{12}]_n$ (233), respectively. Both of these highly air-sensitive compounds have been structurally characterized by x-ray crystallography. The calcium complex contains a $[Ca(CH_3CN)_4]^{2+}$ moiety that caps the hexagonal face of the [*nido*-$C_2B_{10}H_{12}]^{2-}$ cage to complete a 13-vertex polyhedron. The strontium compound, shown in Figure 24**b**, is polymeric and features a $Sr(CH_3CN)_3H_2$ capping moiety, the hydrogen atoms of which are involved in Sr–H–C and Sr–H–B bridging interactions with terminal hydrogen atoms of the carborane cage of adjacent strontium carborane repeating units, producing a spiral polymer chain. Bridging M–H–C interactions are rare in metallacarborane chemistry because B–H groups are generally more basic than C–H groups.

The cogener relationship between boron and aluminum has prompted considerable interest in the aluminacarboranes. The Lewis acid-base adduct 3-(C_2H_5)-3,1,2-$AlC_2B_9H_{11}\cdot 2THF$ was first prepared by the reaction of $Na_2[7,8\text{-}C_2B_9H_{11}]$ and $(C_2H_5)AlCl_2$ in THF solution (235). The reaction of the acidic species *nido*-$C_2B_9H_{13}$ and trialkylaluminum reagents (236) results in loss of one equivalent of alkane and formation of *nido* aluminacarborane species of the type *exo–nido*-9,10-(μ-AlR_2)(μ-H)$_2$-7,8-$C_2B_9H_{10}$ (Fig. 25**b**). Upon heating these species, a second equivalent of alkane is lost with the formation of 12-vertex *closo* aluminacarboranes of the type *closo*-3-R-3,1,2-$AlC_2B_9H_{11}$ (Fig. 24**a**). These two steps can be combined to produce the *closo* aluminacarboranes in a single step:

$$nido\quad 7,8\quad C_2B_9H_{13} + MR_3 \rightarrow closo\quad 3\quad R\quad 3,1,2\quad MC_2B_9H_{11} \tag{77}$$

for M = Al; R = CH_3, C_2H_5; for M = Ga; R = C_2H_5. The same methodology can be applied to the preparation of the corresponding gallacarborane (236). In the absence of Lewis bases, these clusters contain a main group element bound in η^5-fashion to the five-membered face of the dicarbollide cage. The x-ray crystal structure (238) of *closo*-3-(C_2H_5)-3,1,2-$AlC_2B_9H_{11}$ reveals an undistorted icosahedral cluster; however, the ethyl group on aluminum is tilted away from the normal to the plane of the cage bonding face in the direction of the carbon atoms at an angle of 19.4°. This aluminacarborane and its *C*-substituted derivatives form adducts with Lewis bases in which the aluminum atom is slipped dramatically with respect to the dicarbollide cage face in a direction away from the two-carbon atoms (237).

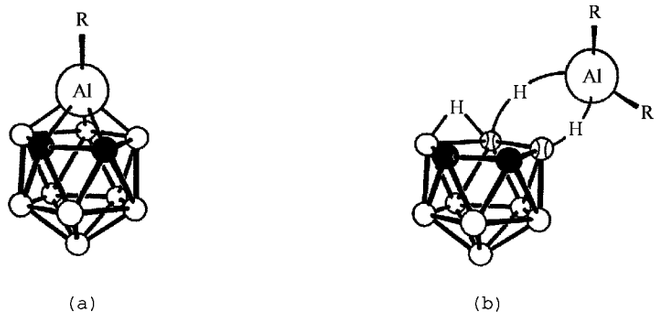


Fig. 25. The molecular structures of (**a**) 3-R-3,1,2-$AlC_2B_9H_{11}$, and (**b**) *exo-nido*-9,10-(μ-AlR_2)(μ-H)$_2$-7,8-$C_2B_9H_{10}$ where ○ represents BH; ●, CH; ⊕, B; and R = CH_3, C_2H_5.

Courtesy of the American Chemical Society (237).

The *closo*-3-(C_2H_5)-3,1,2-$AlC_2B_9H_{11}$ complex is especially interesting because in aromatic solvents it exists in equilibrium with a unique dimer molecule consisting of the $[Al(C_2B_9H_{11})_2]^-$ sandwich ion complexed with a $[(C_2H_5)_2Al]^+$ moiety via two Al–H–B interactions (237). The free $[Al(C_2B_9H_{11})_2]^-$ ion (Fig. 26**a**), in which the aluminum atom is bound in η^5-fashion to the pentagonal faces of two dicarbollide cages, has been isolated and structurally characterized (237,239). The analogous gallacarborane sandwich anion $[Ga(C_2B_9H_{11})_2]^-$ (Fig. 26**b**) has also been characterized and found to possess a significantly distorted structure (237,240). Other aluminacarboranes include $[Al(C_2B_8H_8)_2]^-$, $C_2H_5AlC_2B_8H_{10}$, and $[Al(C_2B_8H_{10})_2]^-$ (237).

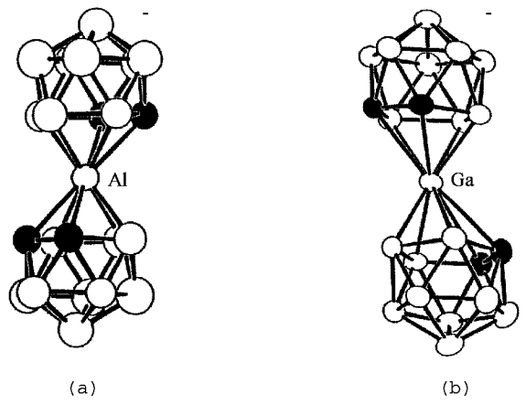


Fig. 26. The x-ray structures of (**a**) [*commo*-3,3′-Al(3,1,2-$AlC_2B_9H_{11})_2$] ;, and (**b**) [*commo*-3,3′-Ga(3,1,2-$GaC_2B_9H_{11})_2$] ;. ○ represents BH; ●, CH.

Courtesy of the American Chemical Society (237).

The thallacarborane anion [*closo*-3,1,2-$TlC_2B_9H_{11}$] ; and its *C*-methyl derivatives are well known (241). The parent anion is prepared by the reaction of *nido*-[$C_2B_9H_{12}$] ; and thallium(I) acetate *[563-68-8]* in aqueous base to give the salt $Tl[TlC_2B_9H_{11}]$, in which one thallium atom caps the dicarbollide cage and the second thallium atom serves as a counterion to the 12-vertex anion. This compound, a yellow, air-stable, insoluble powder, is a convenient synthetic reagent for the preparation of other metallacarboranes. A variety of other thallacarborane salts, eg, $[(C_6H_5)_3PCH_3]$ [3,1,2-$TlC_2B_9H_{11}$] and [PPN] [3,1,2-$TlC_2B_9H_{11}$] where [PPN] $[(C_6H_5)_3P]_2N^+$, can be prepared by cation-exchange reactions using the dithallium compound. The $[PPN]^+$ salt is a useful reagent because of its solubility in organic solvents. Several of these salts have been characterized by x-ray crystallography. The thallium atom of *closo*-[3,1,2-$TlC_2B_9H_{11}$] ; is positioned at the open five-membered face of the dicarbollide cage and is slipped slightly toward the unique boron atom of the cage face. Metal–cage bonding in this anion and its *C*-substituted derivatives has been the subject of some controversy. On one hand the thallium cage atom distances are relatively long, suggesting an ionic interaction. On the other hand, ^1H and ^{11}B nmr spectra show strong coupling between thallium and the cage atoms, indicative of a covalent interaction. The yellow color of the *closo*-[3,1,2-$TlC_2B_9H_{11}$] ; anion has been attributed to metal–cage charge transfer. In some salts, including that of the $[(C_6H_5)_3P]_2N^+$ cation, the solid-state structure of this anion is that of a dimer linked by four Tl–H–B bridging interactions (242).

A series of compounds of the type *closo*-$MC_2B_9H_{11}$ in which M is divalent Ge, Sn, and Pb, have been prepared (243).

$$nido\text{-}[7,8\text{-}C_2B_9H_{11}]^{2-} + MX_2 \rightarrow closo\text{-}3,1,2\text{-}MC_2B_9H_{11} + 2X^- \quad (78)$$

As the B–H group, the 2+ main group atoms act as two-electron donors to the *closo*-$MC_2B_9H_{11}$ cage system. Bonding considerations suggest that these compounds should possess an unshared lone pair of electrons available for bonding at the metal center. However, the complexes do not exhibit Lewis base properties and actually act primarily as Lewis acids, forming donor-acceptor complexes with a variety of donor molecules. The analogous seven-vertex cluster *closo*-$SnC_2B_4H_6$ and its *C*-substituted derivatives form similar donor complexes with Lewis bases. The cluster *closo*-$CH_3GeCB_{10}H_{11}$ (244) has been described. In this compound a Ge–CH_3 moiety, which may be regarded as a three-electron donor, caps a monocarbon carborane cage, to give a twelve-vertex, 26-electron *closo* system. The methyl group on germanium in this compound is reversibly removed by reaction with pyridine to yield the [$GeCB_{10}H_{11}$] ; anion.

The x-ray structure of the novel bis-dicarbollide sandwich compound *commo*-3,3′-Si(3,1,2-$SiC_2B_9H_{11})_2$ contains a silicon atom in a highly unusual bonding mode (245). This compound, which is quite stable thermally, is prepared in good yield.

$$2\,Li_2[7,8\text{-}C_2B_9H_{11}] + SiCl_4 \rightarrow commo\text{-}3,3'\text{-}Si(3,1,2\text{-}SiC_2B_9H_{11})_2 + 4\,LiCl \quad 80\% \quad (79)$$

It is isoelectronic and isostructural with the aluminum sandwich ion [*commo*-3,3′-Al(3,1,2-$AlC_2B_9H_{11})_2$] ; shown in Figure 26**a**. The silicon is η^5-bonded in unslipped fashion to the C_2B_3 faces of two dicarbollide cages. This bis-dicarbollide silicon sandwich also forms adducts of a variety of structural types with Lewis bases such as pyridine and trimethylphosphine.

A series of sandwich compounds of the type *commo*-[{$(CH_3)_3Si$}(R)-$C_2B_4H_4]_2M$, where M is Si, Ge, Sn, and Pb, and R is variously $(CH_3)_3Si$, CH_3, and H, have also been prepared (246). These compounds, formed by reactions between salts of the [{$(CH_3)_3Si$}(R)$C_2B_4H_4]^{2-}$; and [{$(CH_3)_3Si$}(R)$C_2B_4H_5$] ; ions and appropriate main group element halides, have structures containing central main group elements in the 4+ oxidation states similar to the bis-dicarbollide silicon sandwich compound. The structure of the silicon sandwich compound *commo*-[{$(CH_3)_3Si$}$_2C_2B_4H_4]_2Si$ is shown in Figure 27.

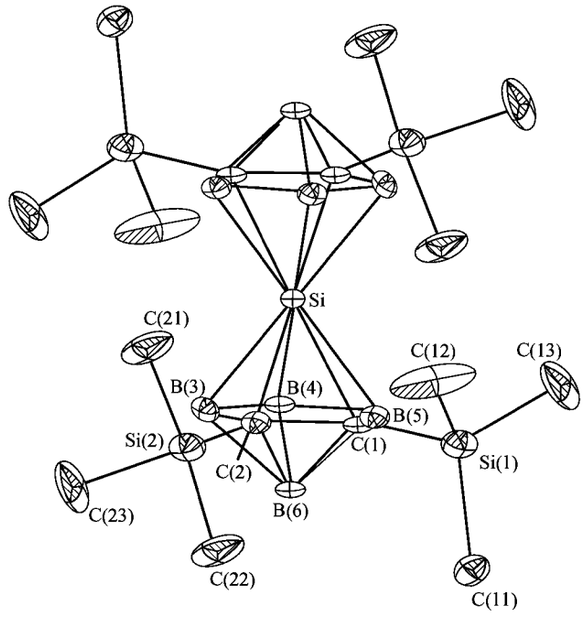


Fig. 27. The x-ray structure of *commo*-2,2′,3,3′-$[(CH_3)_2Si]_4$-*commo*-1,1′-Si(1,2,3-$C_2B_4H_4$).

Courtesy of the American Chemical Society (246).

In compounds of the type *closo*-MC_2B_4H , where M is Ge, Sn, and Pb, the main group elements complete one apex of a pentagonal bipyramid (247). As in the case of the analogous icosahedral clusters, the lone pair of electrons at the divalent main group element center has no tendency to form donor–acceptor complexes with Lewis acids. A number of *C*-substituted compounds of the type *closo*-$MC_2(R)_2B_4H_4$, where M is Si, Ge, Sn, Pb and R is variously H, CH_3, $Si(CH_3)_3$ have also been characterized (248). The x-ray crystal structure of one of the tin-containing members of this series is shown in Figure 28**a**. The compounds in this group react with Lewis bases to form adducts having a variety of intriguing structures, a number of which have been characterized by x-ray crystallography (249). Other smaller main group element carborane derivatives include the seven-vertex gallacarborane cluster *closo*-$CH_3GaC_2B_4H$ (18), shown in Figure 28**b**, which exhibits a tilt distortion of the Ga–CH_3 group similar to that observed for *closo*-3-(C_2H_5)-3,1,2-$AlC_2B_9H_{11}$.

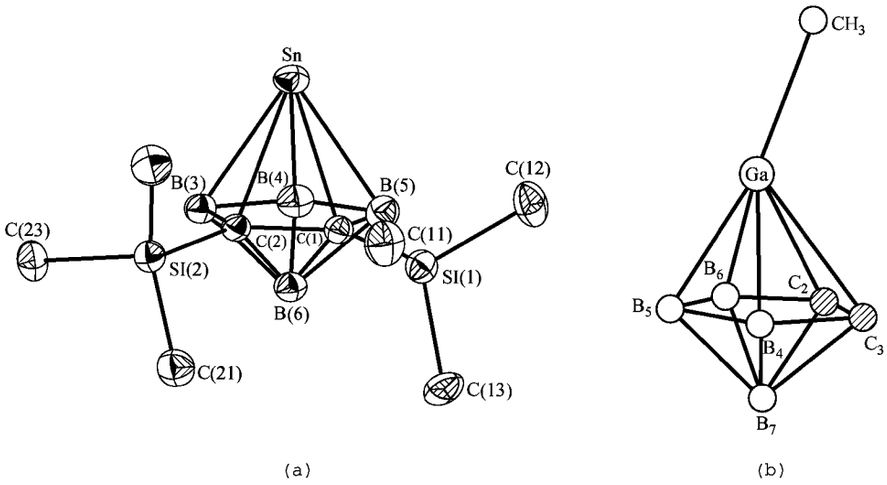


Fig. 28. The x-ray structures of (**a**) 2,3-$[(CH_3)_2Si]_2$-1,2,3-$SnC_2B_4H_4$, and (**b**) 1-CH_3-1,2,3-GaC_2B_4H .

Courtesy of the American Chemical Society (248,18).

A number of related clusters have been prepared based on other heterocarborane cages with faces analogous to $[C_5H_5]$;. These cages include the $[$*nido*-$ECB_9H_{10}]^2$; anions where E P, As, which form metal complexes with many transition and main group elements. *Closo*-$GePCB_9H_{10}$ and *closo*-$GeAsCB_9H_{10}$ are examples (250).

f-Block Element Metallacarborane Derivatives. The first actinide metallacarborane complex, *commo*-$(C_2B_9H_{11})UCl_2$, was prepared in 1977 (251). The coordination geometry of this complex can be described as distorted tetrahedral with the four positions occupied by two η^5-bound $[7,8\text{-}C_2B_9H_{11}]^2$; cages and two chloride ions. Complexes of this type are often referred to as bent sandwiches because of the configuration of the two-dicarbollide cage about the metal center, which is analogous to the corresponding pentamethyl cyclopentadiene–metal complexes.

The synthesis of the first lanthanacarboranes has been described (252). The metathetical reaction of $[$*nido*-$C_2B_9H_{11}]^2$ salts with LnI_2 where Ln Sm or Yb, in THF leads to Ln^{2+} complexes of the type $(C_2B_9H_{11})Ln(THF)_4$ in >55% yield. These complexes, which are stable to temperatures above 200°C, undergo ligand exchange reactions in a variety of donor solvents. The reaction in dimethylformamide (DMF) gives the corresponding $(C_2B_9H_{11})Ln(DMF)_4$ complexes. The structure of the ytterbium complex has been determined to be a *closo* icosahedral cluster consisting of a $C_2B_9H_{11}$ cage capped by an ytterbium atom to which four DMF ligands are coordinated via oxygen. These reactions are similar to those for calcium and strontium metallacarboranes. The reaction of $(C_2B_9H_{11})Sm(THF)_4$ in THF with a soluble salt of the $[$*closo*-3,1,2-$TlC_2B_9H_{11}]$; anion affords the bent samarium sandwich anion, $[$*commo*-$(C_2B_9H_{11})_2Sm(THF)_2]$; (Fig. 29) in 47% yield. The two η^5-dicarbollide cages and two THF ligands are in the coordination sphere of samarium and the average dicarbollide–Sm–dicarbollide angle is 132°. The metal–dicarbollide cage distances found in structurally characterized lanthanacarboranes are

similar to the metal–carbon distances observed for the corresponding lanthanum–pentamethylcyclopentadiene complexes. Neutral monocage complexes of Sm and Yb have also been prepared using the 12-vertex $[nido\text{-}C_2B_{10}H_{12}]^{2-}$ cage.

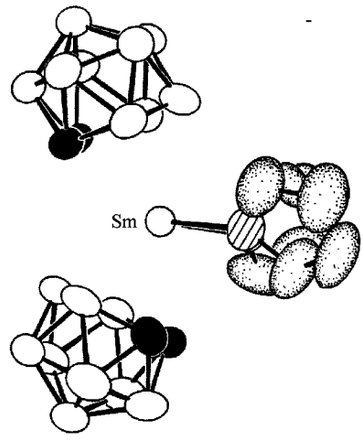


Fig. 29. The x-ray structure of $[3,3\text{-}(C_4H_8O)_2\text{-}commo\text{-}3,3'\text{-}Sm(3,1,2\text{-}SmC_2B_9H_{11})_2]$; where ○ represents BH; ●, CH; ⊘, O; ⊗, CH_2.

Courtesy of the American Chemical Society (252).

Boron Neutron Capture Therapy

One of the most promising applications of polyboron hydride chemistry is boron neutron capture therapy (BNCT) for the treatment of cancers (253). Boron-10 is unique among the light elements in that it possesses an unusually high neutron capture nuclear cross section (3.8×10^{-25} m^2, 0.02–0.05 *e*V neutron). The nuclear reaction between ^{10}B and low energy thermal neutrons yields alpha particles and recoiling lithium-7 nuclei:

$$^{10}_{5}B + {}^{1}n_{th} \longrightarrow [^{11}_{5}B^*] \xrightarrow{94\%} {}^{4}_{2}He + {}^{7}_{3}Li + \gamma \quad (1.47\ MeV,\ 0.84\ MeV,\ 0.48\ MeV) \qquad (80)$$

$$[^{11}_{5}B^*] \xrightarrow{6\%} {}^{4}_{2}He + {}^{7}_{3}Li \quad (1.78\ MeV,\ 1.01\ MeV)$$

2.28 M*e*V is released as kinetic energy.

Because the cytotoxic effects of the energetic lithium-7 and alpha particles are spacially limited to a range of only about one-cell diameter, the destructive effects are confined to only one or two cells near the site of the event. Thus BNCT involves the selective delivery of sufficiently high concentrations of ^{10}B-containing compounds to tumor sites followed by the irradiation of these sites with a beam of relatively nondestructive thermal neutrons. The resulting cytotoxic reaction can then in theory destroy the tumor cells that are intimately associated with ^{10}B target.

It has been estimated that using available neutron intensities such as 10^{12} neutrons ($cm^2 \cdot s$) concentrations of ^{10}B from 10–30 μg/g of tumor with a tumor cell to normal cell selectivity of at least five are necessary for BNCT to be practical. Hence the challenge of BNCT lies in the development of practical means for the selective delivery of approximately 10^9 ^{10}B atoms to each tumor cell for effective therapy using short neutron irradiation times. Derivatives of ^{10}B-enriched *closo*-borane anions and carboranes appear to be especially suitable for BNCT because of their high concentration of ^{10}B and favorable hydrolytic stabilities under physiological conditions.

To date, the most extensively studied polyboron hydride compounds in BNCT research have been the icosahedral mercaptoborane derivatives $Na_2[B_{12}H_{11}SH]$ and $Na_4[(B_{12}H_{11}S)_2]$, which have been used in human trials with some, albeit limited, success. New generations of tumor-localizing boronated compounds are being developed. The dose-selectivity problem of BNCT has been approached using boron hydride compounds in combination with a variety of delivery vehicles including boronated polyclonal and monoclonal antibodies, porphyrins, amino acids, nucleotides, carbohydrates, and liposomes. Boron neutron capture therapy has been the subject of recent reviews (254).

A related potential medical application of metallacarboranes is based on the highly favorable kinetic stability of many metallacarborane complexes under physiological conditions. This feature makes certain functionalized metallacarboranes containing radiometals ideal choices for use as medical imaging reagents (see IMAGING TECHNOLOGY). The use of antibody-conjugated bridged dicarbollide metallacarborane (venus fly trap) chelate complexes incorporating gamma-emitting $^{57}Co^{3+}$ in the imaging tumors has been reported (255).

Economic Aspects

Despite the fact that many boron hydride compounds possess unique chemical and physical properties, very few of these compounds have yet undergone significant commercial exploitation. This is largely owing to the extremely high cost of most boron hydride materials, which has discouraged development of all but the most exotic applications. Nevertheless, considerable commercial potential is foreseen for boron hydride materials if and when economical and reliable sources become available. Only the simplest of boron hydride compounds, most notably sodium tetrahydroborate, $Na[BH_4]$, diborane(6), B_2H_6, and some of the borane adducts, eg, amine boranes, are now produced in significant commercial quantities.

Sodium Tetrahydroborate, $Na[BH_4]$. This air-stable white powder, commonly referred to as sodium borohydride, is the most widely commercialized boron hydride material. It is used in a variety of industrial processes including bleaching of paper pulp and clays, preparation and purification of organic chemicals and pharmaceuticals, textile dye reduction, recovery of valuable metals, wastewater treatment, and production of dithionite compounds. Sodium borohydride is produced in the United States by Morton International, Inc., the Alfa Division of Johnson Matthey, Inc., and Covan Limited, with Morton International supplying about 75% of market. More than six million pounds of this material supplied as powder, pellets, and aqueous solution, were produced in 1990.

Diborane(6), B_2H_6. This spontaneously flammable gas is consumed primarily by the electronics industry as a dopant in the production of silicon wafers for use in semiconductors. It is also used to produce amine boranes and the higher boron hydrides. Callery Chemical Co., a division of Mine Safety Appliances Co., and Voltaix, Inc., are the main U.S. producers of this substance. Several hundred thousand pounds were manufactured worldwide in 1990.

Amine Boranes. Trialkylamine and dialkylamine boranes, such as tri-*t*-butylamine borane and dimethylamine borane, are mainly used in

electroless plating processes. They are produced by Callery Chemical Co.

Polyhedral Boron Hydrides. Although relatively large quantities of polyhedral boron hydrides and carboranes have been produced under various government contracts, these materials are not currently produced on a regular commercial basis. Pentaborane(9) (*nido*-B_5H_9) and decaborane(14) (*nido*-$B_{10}H_{14}$), and carboranes, such as the ortho and meta-carboranes *closo*-1,2-$C_2B_{10}H_{12}$ and *closo*-1,7-$C_2B_{10}H_{12}$, as well as various other derivatives, are available in experimental quantities. Prices for these compounds range, according to purity, composition, and quantity purchased, from $4,000 to $25,000 or more per kilogram. Callery Chemical Co. has the capability to produce these materials on demand.

Demonstrated areas of potential commercial applications for other boron hydride-based materials are listed according to the classes of these materials.

Polyhedral Boron Hydrides. These are used in neutron capture therapy of cancers (254), and as burn rate modifiers (accelerants) in gun and rocket propellant compositions.

Carboranes. These are used in neutron capture therapy (254), and as burn rate modifiers in gun and rocket propellants. They are used as high temperature elastomers and other unique materials, high temperature gas–liquid chromatography stationary phases, optical switching devises (256), and gasoline additives (257).

Metallacarboranes. These are used in homogeneous catalysis (222), including hydrogenation, hydrosilylation, isomerization, hydrosilanolysis, phase transfer, burn rate modifiers in gun and rocket propellants, neutron capture therapy (254), medical imaging (255), processing of radioactive waste (192), analytical reagents, and as ceramic precursors.

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BORON HYDRIDES, HETEROBORANES, AND THEIR METALLA DERIVATIVES (COMMERCIAL ASPECTS)

Boranes, B–H-containing compounds, having proven commercial value are the tetrahydroborates, several borane complexes, and some hetereoboranes.

Tetrahydroborates

Sodium tetrahydroborate *[16940-66-2]*, $NaBH_4$, more commonly called sodium borohydride, is the most widely used commercial boron hydride. The largest manufacturer is Morton International Specialty Chemicals Group, which has two plants in the United States and one in Europe (1). Oy Nokia Ab Chemicals (FN) (2) also produces commercial quantities. Smaller producers include Farbenfabrik Bayer A.G. and Chemetall Gmbh in Germany (2).

Sodium borohydride is available as a 12% solution in caustic soda and in solid form either as powder or pellets (3). The predominant form produced is the solution, the DOT shipping classification for which is corrosive liquid. Forms of packaging are 18.9-L pails, 208.2-L drums, and either tank truck or tank car for bulk shipments. 1991 pricing for the solution form was $40.34 kg of borohydride contained. Solid sodium borohydride, a white powder packaged in polyethylene bags in metal containers, was priced at $48.39 kg.

Solid sodium borohydride does not ignite upon contact with moisture and is not shock sensitive. These characteristics allow it to be handled safely in air. Because it does liberate hydrogen upon contact with water it should be handled with care.

The predominant use for sodium borohydride is in wood pulp (qv) bleaching (4–7). The next largest commercial use is as a reducing agent of functional groups in organic synthesis (3). Examples are the reduction of aldehydes (qv) and ketones (qv) to the corresponding alcohols. A significant application in pharmaceutical synthesis is the stereospecific and selective reduction in steroid production (8). Other commercial applications include control of odors in alcohols (9), decolorization of ketones (10) and polyols (11), and electroless plating (qv) of nickel (12), gold (13,14), and other metals for electronic and aerospace applications. An important application is the removal of toxic or heavy metals from process waste streams and spent plating solutions (15–17).

Sodium borohydride reacts with Lewis acids in nonprotic solvents to yield diborane *[19287-45-7]*, B_2H (18), which can then be used to generate other useful organoboranes such as amine boranes, alkyl boranes, and boron hydride clusters.

Other tetrahydroborates of less commercial importance are lithium borohydride *[16949-15-8]*, $LiBH_4$, and potassium borohydride *[13762-51-1]*, KBH_4.

Borane Complexes

Borane complexes are the most widely used commercial boron compounds, after sodium borohydride. Examples used in organic synthesis are amine borane complexes and borane complexes of tetrahydrofuran and dimethyl sulfide.

Dimethylamine borane *[74-94-2]*, $C_2H_7N \cdot BH_3$, *t*-butylamine borane *[7337-45-3]*, $C_4H_{11}N \cdot BH_3$, and pyridine borane *[110-51-0]*, $C_5H_5N \cdot BH_3$, are the most common amine borane complexes. The stability, ease of handling, solubility in a variety of protic and aprotic solvents, and ability to chemo- and stereoselectively reduce aldehydes and ketones (19–21) of these complexes has lead to their use as reducing agents in organic synthesis. Other applications include the development of photographic film and electroless plating (22–24) of metals such as Cu, Ni, and Au.

Tetrahydrofuran borane *[14044-65-6]*, $C_4H_8O \cdot BH_3$, and dimethyl sulfide borane *[13292-87-0]*, $C_2H_6S \cdot BH_3$, have found use in organic synthesis as reducing agents and hydroborating agents (25,26). Diisopinocampheylchloroborane *[85116-37-6]*, $C_{20}H_{34}BCl$ (27) and oxazaborolidines, C_2H_4BNORR' (28) are important reagents for chiral synthesis.

Potential Uses of $B_{12}H_{11}SH^{2-}$. Although not commercial as yet, an interesting potential use of borane compounds as therapeutic agents for the treatment of inoperable cancerous tumors is being developed (see CHEMOTHERAPEUTICS, ANTICANCER). Boron neutron capture therapy (bnct) involves the uptake of boron compounds enriched with the boron-10 *[14798-12-0]*, ^{10}B, isotope, selectively accumulating in cancerous tumors (29). Low energy thermal or epithermal neutrons penetrate healthy tissue, reacting with ^{10}B in the tumor releasing an alpha particle. This high energy alpha particle selectively destroys the tumor cells. One particular borane, disodium mercaptoundecahydrododecaborate *[12448-24-7]*, $Na_2B_{12}H_{11}SH$, can across the blood–brain barrier and is taken up by Grade IV glioblastomas (brain tumors). This borane has been used in Japan (30) to treat tumors clinically. Other tumors, such as malignant melanoma (31), are being treated with borono-phenylalanine *[74923-16-3]*, $(OH)_2{}^{10}BC_6H_4CH_2CHNH_2COOH$, a boron containing amino acid. There is also research into using boron containing macromolecules such as borated monoclonal antibodies or borated porphrins for treatment of other tumors (32).

Heteroboranes

Heteroboranes, compounds where one or more of the cage borons are replaced by a main group element (33), are not themselves commercially available. However, carborane siloxanes containing *m*-carborane *[16986-21-6]*, $C_2H_{12}B_{10}$, are available under the trade name of Dexsil for the stationary phase in gas–liquid chromotography (qv) (34). The carborane, 1,7-dicarba-*closo*-dodecaborane(10) (35), contributes enhanced chemical and thermal stability to the siloxane polymer.

Potential areas of application for carboranes include adhesives, gaskets, and O-rings (27). Research has been reported on improving the oxidation resistance and strength of carbon materials by coating with a carborane siloxane polymer (36).

Two alkyl derivatives of the $C_2B_{10}H_{12}$ carboranes were developed for propellant additives: *n*-hexyl carborane (*n*HC) *[20740-05-0]*, $C_2B_{10}H_{11}C_6H_{13}$ (37–39) and carboranyl methyl propionate (CMP) *[62906-37-0]*, $C_2B_{10}H_{11}CH_2O_2CCH_2CH_3$ (40). These two carboranes can be synthesized from decaborane(14), $B_{10}H_{14}$. Decaborane(14) *[17702-41-9]*, $B_{10}H_{14}$, has been synthesized from diborane (9), pentaborane *[19624-22-7]*, B_5H_9 (41–43) and sodium borohydride (44). At the manufacturing level, a pyrolitic process to produce decaborane from diborane has been reported (45). A production plant having the capacity to produce ton qualities of *n*HC from decaborane(14) was operated in the 1980s for the U.S. Army. The production of CMP and other derivatives of decaborane(14) are also feasible in this plant which is inactive as of this writing.

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ORGANIC BORON–NITROGEN COMPOUNDS

The first attempt to systematize the field of BN-containing organic compounds was made in 1948 (1,2) upon recognition of the isoelectronic relationship between B–N and C–C moieties. There are four classes of organic B–N compounds. (*1*) Amine boranes, $R_3B{-}NR'_3$, have the nitrogen atom which supplies both electrons in the B–N bond; these are isoelectronic with alkanes, $R_3C{-}CR'_3$. (*2*) Aminoboranes, $R_2B{=}NR'_2$, have a covalent bond between B and N. Here, the hybridization of both boron and nitrogen is sp^2 resulting in a planar $R_2BNR'_2$ unit capable of a π-interaction between nitrogen's free-electron pair and the empty *p* orbital on boron; these are isoelectronic with alkenes, $R_2C{=}CR'_2$. (*3*) Iminoboranes, $RB{\equiv}NR'$, have a two-coordinate boron interacting with the nitrogen via a triple bond; these are isoelectronic with alkynes, $RC{\equiv}CR$. (*4*) Borazines, $(-RB{-}NR'-)_x$, are cyclic compounds containing alternating tricoordinate boron and nitrogen atoms. These compounds are nearly planar and have B–N bond lengths that are substantially shorter than those for single bonds, indicating partial double-bond character. Borazines are isoelectronic with benzene, C_6H_6. There are also B–N ring systems of other sizes. Although these compounds are isoelectronic and nearly isostructural with conventional organic species, properties and reactivity patterns are considerably different. The primary reason for this dissimilarity is the polar nature of the B–N bond.

Reviews covering the literature through 1970 for all areas except iminoboranes (3) and through 1984 (4) are available.

Amine Boranes

Amine–borane adducts have the general formula $R_3N{\cdot}BX_3$ where R = H, alkyl, etc, and X = alkyl, H, halogen, etc. These compounds, characterized by a coordinate covalent bond between boron and nitrogen, form a class of reducing agents having a broad spectrum of reduction potentials (5).

Synthesis. An efficient, convenient synthesis for the preparation of ammonia borane *[13774-81-7]*, the inorganic analogue of ethane, is shown in equation 1 where THF is tetrahydrofuran (6).

$$(NH_4)_2CO_3 + 2\,NaBH_4 \xrightarrow{\text{anhydrous THF}} 2\,H_3N{\cdot}BH_3 + 2\,H_2 + Na_2CO_3 \tag{1}$$

A synthesis using liquid ammonia and $NaBH_4$ has also been described (7). Both methylamine borane *[1722-33-4]*, $(CH_3)H_2N{\cdot}BH_3$, and ethylamine borane *[15860-41-0]*, $(C_2H_5)H_2N{\cdot}BH_3$, can also be prepared in this manner.

Dimethylamine borane *[74-94-2]*, important as a reducing agent in electroless plating (qv) (8), can be synthesized as shown in equation 2 (9).

$$(CH_3)_2NH_2Cl + NaBH_4 \xrightarrow[\text{RT}]{\text{ether}} (CH_3)_2HN{\cdot}BH_3 + H_2 + NaCl \tag{2}$$

Pyridine borane *[110-51-0]* can be prepared using benchtop techniques via

$$C_5H_5N + THF{\cdot}BH_3 \xrightarrow[0^\circ C]{\text{THF}} \underset{\text{excess}}{C_5H_5{\cdot}BH_3} \tag{3}$$

The synthesis of a number of other amine–borane complexes from $THF{\cdot}BH_3$ *[14044-65-6]* have also been described (10).

Using a procedure similar to the synthesis of amine boranes, a series of amine cyanoboranes where the amine = $(CH_3)_3N$, $(CH_3)_2NH$, $(CH_3)NH_2$, C_5H_5N, or $(C_6H_5)NH_2$ have been prepared as shown in equation 4 (11).

$$NaBH_3CN + \text{amine-HCl} \xrightarrow[65^\circ C]{\text{THF}} \text{amine-}BH_2CN + H_2 + NaCl \tag{4}$$

Trimethylamine carboxyborane can be synthesized from the cyanoborane precursor *[30353-61-8]* according to equations 5 and 6 (12).

$$(CH_3)_3N{\cdot}BH_2CN + (C_2H_5)_3O^+BF_4 \xrightarrow[\Delta]{CH_2Cl_2} (CH_3)_3N{\cdot}BH_2CN(C_2H_5)^+BF_4 + (C_2H_5)_2O \tag{5}$$

$$(CH_3)_3N{\cdot}BH_2CN(C_2H_5)^+BF_4 + 2\,H_2O \rightarrow (CH_3)_3N{\cdot}BH_2COOH + (C_2H_5)NH_3^+BF_4 \tag{6}$$

This carboxyborane can undergo an amine exchange reaction with liquid ammonia (eq. 7) to yield the boron analogue of glycine, the simplest alpha-amino acid (13). There has been a great deal of work on the pharmacological activity of these amino acid analogues (14).

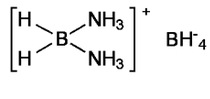
$$(CH_3)_3N{\cdot}BH_2COOH + NH_3 \rightarrow H_3N{\cdot}BH_2COOH + N(CH_3)_3 \tag{7}$$

Compounds of the type $L{\cdot}BH_2X$ can be prepared by the reaction of the appropriate amine borane and hydrogen halides or halogens. The synthesis of the trimethylamine iodoborane *[25741-81-5]* adduct (eq. 8) yields a precursor for the preparation of the trimethylamine isocyanoborane *[60045-36-5]* adduct as shown in equation 9 (15).

$$2\,(CH_3)_3N{\cdot}BH_3 + I_2 \rightarrow 2\,(CH_3)_3N{\cdot}BH_2I + H_2 \tag{8}$$

$$(CH_3)_3N{\cdot}BH_2I \xrightarrow{AgCN,\ H_2S} (CH_3)_3N{\cdot}BH_2(NC) + AgI \tag{9}$$

Amine–Boronium Cations. The most extensively studied boronium cation is the diammoniate of diborane *[23777-63-1]* (16–18).



In this compound, synthesized in the low temperature reaction between diborane and excess ammonia, the cationic boron is coordinatively saturated in a tetrahedral environment. More recently, cations having boron in tricoordinate or dicoordinate environments have been observed. These cationic species, called borenium and borinum ions, respectively, have been reviewed (19,20).

Properties and Reactions. Amine boranes are usually colorless, crystalline compounds, which exhibit sharp melting points and thermal stability when pure. Primary and secondary amine boranes are generally solids at ambient temperatures. With the exception of trimethylamine borane, the aliphatic *t*-amine boranes are liquids. The nature of the bonding in amine boranes has been the subject of theoretical investigations (21–23). Representations of the bonding have used symbols such as $R_3N \rightarrow BX_3$ or $R_3N^+ \quad BX_3^-$ to indicate the direction of charge-transfer and origin of the bonding electrons. These symbols refer to the relative change in electron density with respect to the individual precoordination donor and acceptor molecules, not to charges on N and B in the adduct. Molecular orbital calculations indicate that the change in electron density upon coordination reduces, but is insufficient to reverse, the initial positive charge on boron that is a consequence of the differences in electronegativity between B and N. Experimental results are consistent with this representation: nucleophilic reagents always attack B in amine–borane complexes, electrophilic reagents preferentially attack N.

Amine boranes have been examined by a variety of spectroscopic methods (24–29). The boron-substituted alpha-amino acids have been utilized in animal model studies. These compounds along with their precursors and selected derivatives have been shown to possess antineoplastic, antiarthritic, and hypolipidemic activity (30–32). The boron amino acid analogues are also being evaluated for possible utility in boron neutron capture therapy (BNCT) (33).

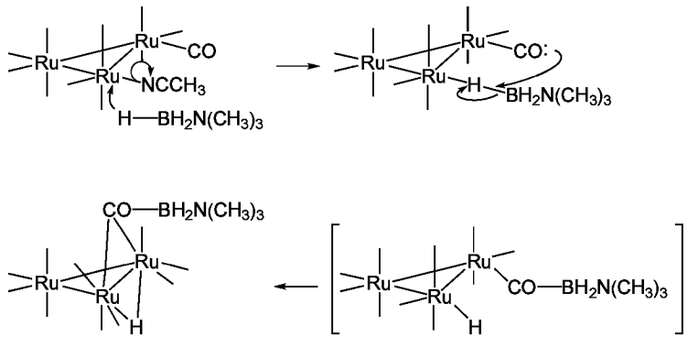
Amine–borane complexes are widely used as reducing agents in organic and inorganic chemistry; examples of reactions are available (8,34,35). Compared to sodium borohydride they offer good solubility in organic solvents and are less sensitive to acids but are generally weaker reducing agents. The reduction of cyclohexanone using a variety of amine–BH_3 complexes has been investigated (10) and a mechanism involving prior dissociation of the amine borane was proposed. A similar reaction pathway has been proposed for the hydroboration of alkenes using amine–BH_3 complexes (36).

The influence of boron-bonded ligands on the kinetics and mechanistic pathways of hydrolysis of amine boranes has been examined (37,38). The stoichiometry of trimethylamine azidoborane *[61652-29-7]* hydrolysis in acidic solution is given in equation 10. It is suggested that protonation occurs at the azide ligand enabling its departure as the relatively labile HN_3 species.

$$(CH_3)_3N{\cdot}BH_2N_3 + H^+ + 3\,H_2O \rightarrow (CH_3)_3NH^+ + B(OH)_3 + 2\,H_2 + HN_3 \tag{10}$$

A series of metal complexes containing trimethylamine boranecarboxylato ion ligand *[103904-11-6]*, $(CH_3)_3N{\cdot}BH_2COO^-$, have been prepared with Co(III), Co(II), Zn(II), Ca(II), Cr(III), and Fe(III) (39,40). This ligand, derived from the boron analogue of the amino acid glycine, behaves similarly to organic carboxylato ligands.

The reaction between a trinuclear metal carbonyl cluster and trimethylamine borane has been investigated (41) and here the cluster anion functions as a Lewis base toward the boron atom, forming a B–O covalent bond (see CARBONYLS). Molecular orbital calculations, supported by structural characterization, show that coordination of the amine borane causes small changes in the trinuclear framework.



Aminoboranes

The aminoboranes are characterized by a normal covalent bond between boron and nitrogen in which an electron from each atom is shared. In this case the hybridization of both boron and nitrogen is sp^2, resulting in a planar moiety capable of π-interaction by utilizing the nitrogen's free-electron pair and boron's vacant *p* orbital. There exists a wide variety of aminoborane compounds; among those that have been thoroughly investigated are the monoaminoboranes X_2BNR_2, bisaminoboranes $XB(NR_2)_2$, and trisaminoboranes $B(NR_2)_3$. The substituents X and R may vary widely, but generally R is an alkyl or aryl group, or hydrogen, whereas X can represent a rather wide variety of atoms or groups. There also exist aminoborane compounds, which have multiple boron substituents bonded to a single nitrogen; such as the diborylamines $X_2B{-}NR{-}BX_2$ and the triborylamines $(X_2B)_3N$. Coordinative saturation in aminoboranes can be achieved not only through partial double-bond formation (π-interaction) but also by association (usually dimerization) of the monomeric units. The presence of bulky groups on either B or N hinders dimer formation. In general, the monomeric compounds are more reactive than the associated species.

Synthesis. One of the more common routes for the synthesis of aminoboranes involves the aminolysis of the appropriate boron halide. Trisaminoboranes are most conveniently prepared by adding BCl_3 to an excess of amine in an inert solvent at low temperatures (42). For example for tris(dimethylamino)borane *[4375-83-1]*:

$$BCl_3 + 6\,HN(CH_3)_2 \xrightarrow[80^\circ C]{\text{pentane}} [(CH_3)_2N]_3B + 3\,(CH_3)_2NH_2Cl \tag{11}$$

A widely used reaction for preparing unsymmetrical aminoboranes is the treatment of an aminoborane $B(NR_2)_3$ with another boron compound BX_3 to induce an exchange of the substituents; an example is given in equation 12 (43).

$$2\,B(C_2H_5)_3 + B[N(C_2H_5)_2]_3 \xrightarrow[120^\circ C]{\text{catalyzed } H_3B\ THF} 3\,(C_2H_5)_2BN(C_2H_5)_2 \tag{12}$$

Here diethylaminodiethylborane *[4023-39-6]* is obtained in nearly quantitative fashion (97%). The novel trifluoromethylaminoboranes $CF_3(X)BN(C_2H_5)_3$, where X = Cl *[126810-68-2]*, Br *[126827-53-0]*, have been prepared (44).

$$[(C_2H_5)_2N]_3P + CF_3Br + X_2BN(C_2H_5)_2 \rightarrow CF_3(X)BN(C_2H_5)_2 + [(C_2H_5)_2N]_3PX^+Br^- \tag{13}$$

The stability toward additional disproportionation is dependent on the increase in B–N bond strength as well as steric effects resulting from the R group.

The chemistry and stereochemistry of aminoboranes containing the silicon–nitrogen–boron linkage have been the subject of numerous studies. Many of these compounds are useful precursors to other B–N systems including diboryl-amines (45) and B–H substituted aminoboranes (46). A series of

alkyl[bis(trimethylsily)amino]boranes have been prepared by alkylating $((CH_3)_3Si)_2NBCl_2$ *[6591-26-0]* using the appropriate organometallic reagent (47). For example:

$$[(CH_3)_3Si]_2NBCl_2 \xrightarrow[C_2H_5O,\ 0°C]{t\text{-}C_4H_9} [(CH_3)_3Si]_2NB\begin{matrix} t\text{-}C_4H_9 \\ Cl \end{matrix} \qquad (14)$$

The *t*-butyl derivative *[87487-06-9]* reacts with ammonia as shown in equation 15 to yield a stable primary aminoborane *[99748-68-2]* (48). The stability of primary aminoboranes has been attributed to the presence of a bulky substituent on boron (49).

$$[(CH_3)_3Si]_2NB\begin{matrix} t\text{-}C_4H_9 \\ Cl \end{matrix} + 2\ NH_3 \xrightarrow{\text{hexane}} [(CH_3)_3Si]_2NB\begin{matrix} t\text{-}C_4H_9 \\ NH_2 \end{matrix} + NH_4Cl \qquad (15)$$

This primary aminoborane is a useful reagent for attaching B–N moieties to other elements, eg, (borylamino)phosphines, or for extending short B–N chains, eg, diborylamines.

A series of lithium complexes have been utilized as synthons in the preparation of aminoborane complexes. (*N*-Lithiomethylamino)dimethylborane is used as a reagent for the preparation of borylamino(amino)boranes and diborylamines (50). Lithium benzyl-*tert*-butylamide reacts with BCl_3 to yield the bisaminoborane *[91573-50-1]* shown in equation 16 (51).

$$3\ LiN\begin{matrix} C(CH_3)_3 \\ CH_2C_6H_5 \end{matrix} + BCl_3 \longrightarrow HB\left[N\begin{matrix} C(CH_3)_3 \\ CH_2C_6H_5 \end{matrix}\right]_2 + 3\ LiCl + (CH_3)_3CN \quad {=}CHC_6H_5 \qquad (16)$$

Both symmetrically and unsymmetrically substituted diborylamines can be prepared using sterically demanding *N*-lithioaminoboranes (52).

Properties and Reactions. Monoaminoboranes readily undergo association, the extent of which primarily depends on the steric requirements of the groups attached to boron and nitrogen. The monomers are generally liquids or low melting solids whereas the dimers and trimers are crystalline solids. The bis- and trisaminoboranes do not show a tendency to dimerize, and are also less sensitive to hydrolysis than the monomeric monoaminoboranes; they are generally high boiling liquids or crystalline solids.

The bonding in aminoboranes has been represented as $X_2N^+ \text{---} BR_2$ or $X_2N \dashrightarrow BR_2$ to show the contribution of some π-orbital interaction between the lone pair on N and the vacant orbital on trigonal boron. As with the amine–borane adducts this does not necessarily indicate net charges on N and B. The greater electronegativity of N should cause the sigma bond to be polarized in the opposite sense. Calculations carried out on the pure inorganic aminoborane, H_2NBH_2, however, indicate a covalent π-bond, producing positive charge on N, negative on B (53–55). The sp^2 hydridization of both boron and nitrogen lead to planar X_2BNR_2 fragments with the contribution of a π-interaction being supported by B–N separations of ca 0.14 nm as compared to a B–N bond distance of ca 0.16 nm in amine boranes.

In aminoboranes there is a barrier to rotation about the boron–nitrogen bond resulting from the high B–N bond order. There have been numerous studies carried out using variable-temperature nmr to obtain activation parameters for restricted rotation about the B–N bond (56–59). The steric effects of the substituents was shown to be the principal factor affecting the barrier. In general, monoaminoboranes all have rather high rotational barriers 71–100 kJ mol (17–24 kcal mol). Multinuclear nmr has been used to determine the coupling constants in aminoboranes (60,61). The vibrational spectra of bis(dimethylamino)boranes have been examined (62).

Monoaminoboranes containing hydrogen attached to nitrogen, and hydrogens or halogens bonded to boron undergo an internal elimination reaction on heating, yielding borazines (63). Bisaminoboranes in general are thermally stable; when pyrolysis does occur a principal reaction product is a borazine as illustrated in equation 17 (64).

$$3\ (C_2H_5NH)_2BH \rightarrow (\text{—}BH\text{—}NC_2H_5\text{—})_3 + 3\ C_2H_5NH_2 \qquad (17)$$

The emphasis in the approaches to boron nitride *[10043-11-5]*, BN, precursors has been concentrated on cyclic compounds. There have been recent reports of trimethylsilyl-substituted aminoboranes being evaluated as B–N precursors. These are linear borylamines containing up to four boron atoms. Compounds were also synthesized with free $-NH_2$ groups amenable to condensation with either dihaloboranes or dihaloborazines (65) and offering suitable monomers for linear B–N polymer synthesis and borazine-ring-linking applications.

Aminoboranes have been used as ligands in complexes with transition metals (66); in one instance giving a rare example of two-coordinate, non-d^{10} transition-metal complexes. The molecular structure of the iron complex $Fe[N(Mes)B(Mes)_2]_2$ where Mes 2,4,6-$(CH_3)_3C\ H_2$ is shown in Figure 1. The less sterically demanding lithium borylamide, $LiN(CH_3)B(CH_3)_2$, used to prepare mercury and tin complexes, has also been prepared (67).

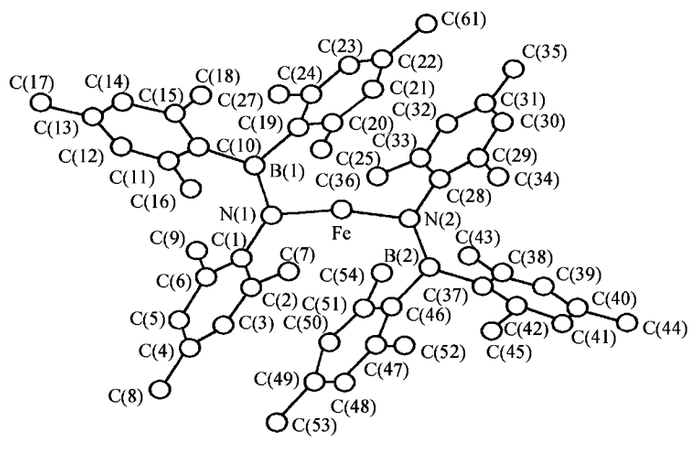


Fig. 1. Structure of $Fe[N(Mes)B(Mes)_2]_2$ where Mes is 2,4,6-$(CH_3)_3C\ H_2$.

The reduction of (alkylamino)haloboranes using hydride reagents can provide a convenient route to (alkylamino)boranes: for example, $LiAlH_4$ has been utilized to prepare bis(dimethylamino)borane *[23884-11-9]* from chlorobis(dimethylamino)borane *[6562-41-0]* (68). When this same strategy is applied to (bis(trimethylsilyl)amino)chloro((trimethylsilyl)amino)borane *[10078-93-0]*, the expected compound is obtained along with the formation of two

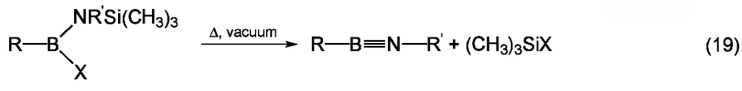
borazine derivatives (69).

$$[(CH_3)_3Si]_2NB(Cl)N(H)Si(CH_3)_3 \xrightarrow{LiBH_4} [(CH_3)_3Si]_2NBH_2 + [(CH_3)_3SiN(H)BH_2]_3 + [(CH_3)_3SiNBH]_3 \quad (18)$$

Iminoboranes

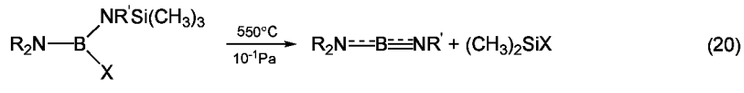
A new class of boron–nitrogen compounds was reported in 1975 when the first iminoborane having two-coordinate boron, $(C_6F_5)B{\equiv}N(t\text{-}C_4H_9)$ *[72886-65-8]*, was isolated (70). Since then more than 50 iminoboranes have been synthesized and characterized. Iminoboranes, XBNR, are isoelectronic with alkynes, XCCR. Whereas the structural and physical properties of these species are rather parallel, this similarity does not hold for reactivity. The polarity of the B–N bond makes iminoboranes much more reactive than the analogous XCCR species. Comprehensive reviews of iminoboranes may be found in the literature (71,72). A class of B–N compounds with a *sp*-hybridized nitrogen attached to a three-coordinated boron, $R_2C{=}N{-}BX_2$, have also been classified as iminoboranes (73–75).

Synthesis. Iminoboranes, thermodynamically unstable with respect to oligomerization can be isolated under laboratory conditions by making the oligomerization kinetically unfavorable. This is facilitated by bulky substituents, high dilution, and low temperatures. The vacuum gas-phase pyrolysis of (trimethylsilylamino)(alkyl)haloboranes has been utilized as an effective method of generating iminoboranes $RB{\equiv}NR'$ as shown in equation 19 for X = F, Cl, Br, and OCH_3 (72).



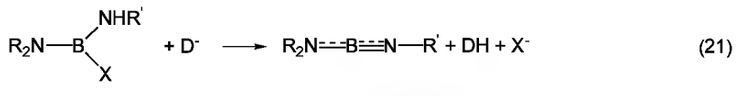
(19)

The products are trapped at liquid nitrogen temperature. This strategy can also be employed in the synthesis of amino iminoboranes (76), where X = F, Cl.



(20)

Iminoboranes have been suggested as intermediates in the formation of compounds derived from the pyrolysis of azidoboranes (77). The intermediate is presumed to be a boryl-substituted nitrene, RR′BN, which then rearranges to the amino iminoborane, neither of which has been isolated (78). Another approach to the synthesis of amino iminoboranes involves the dehydrohalogenation of mono- and bis(amino)haloboranes as shown in equation 21. Bulky alkali-metal amides, MNR_2, have been utilized successfully as the strong base, D⁻, in such a reaction scheme. Use of lithium-*tert*-butyl(trimethylsilyl)amide yields an amine, DH, which is relatively volatile (76,79).



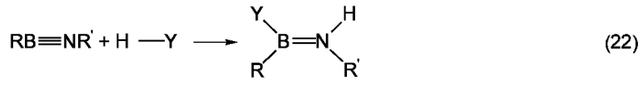
(21)

Properties and Reactions. The structure of (alkyl)iminoboranes $RB{\equiv}NR'$ is characterized by a linear C–B–N–C geometry and a B–N bond order approaching three. Amino iminoboranes can be described using three resonance structures:

$$\underset{}{R_2N{-}B{\equiv}NR'} \leftrightarrow \underset{A}{R_2N{=}B{-}NR'} \leftrightarrow \underset{B}{R_2N{-}B{=}NR'} \quad \underset{C}{}$$

The boron atoms in resonance structures A and B possess a formal negative charge. The simplest representation for these compounds is $R_2N{---}B{\equiv}NR'$. The relative stability of iminoboranes and amino iminoboranes shows strong dependence on the steric bulk offered by R and R′. This is illustrated by the stability of $t\text{-}C_4H_9B{\equiv}Nt\text{-}C_4H_9$ at 0°C whereas the permethyl analogue, $(CH_3)B{\equiv}N(CH_3)$, decomposes above −110°C (72). The high B–N bond order in iminoboranes has been verified by the results of single-crystal x-ray structure determinations: there is a B–N separation of 0.122 nm in $[(CH_3)_3Si]_3Si{-}B{\equiv}N{-}t\text{-}C_4H_9$ (80). Spectroscopic characterization of these compounds has been carried out at low temperature using ^{11}B nmr and ir spectroscopy (81).

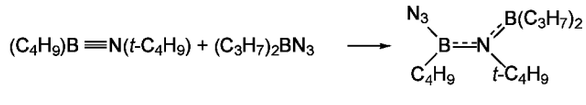
The chemistry of these compounds reflects the unsaturated nature of the B–N triple bond. Polar compounds add to iminoboranes, provided the addition proceeds more rapidly than oligomerization of $RB{\equiv}NR'$ (82). For example, for R = R′ = $CH(CH_3)_2$ or $t\text{-}C_4H_9$.



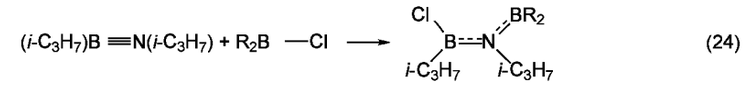
(22)

where HY = HCl, $t\text{-}C_4H_9OH$, $(C_2H_5)_2NH$, $(i\text{-}C_3H_7)_2NH$, $t\text{-}C_4H_9NH_2$, $((CH_3)_3Si)_2NH$.

In an analogous fashion to the hydroboration reaction, a variety of boron-containing substrates react with iminoboranes. Addition of $X_2B{-}Cl$, $X_2B{-}N_3$, $X_2B{-}SR$, $X_2B{-}NR_2$, and $X_2B{-}R$ to the unsaturated B–N system is called chloro-, azido-, thio-, amino-, and alkyloboration, respectively. The azidoboration and chloroboration of two iminoboranes are shown in equations 23 and 24 (72).

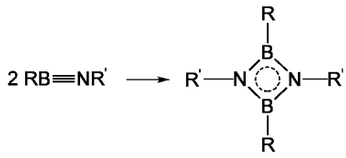


(23)



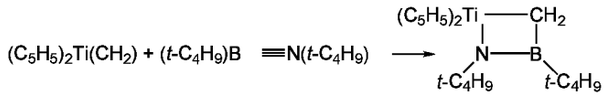
(24)

A general type of stabilization for iminoboranes is a cyclodimerization, which yields diazadiboretidines $(RBNR')_2$ that are isoelectronic with cyclobutadienes.



(25)

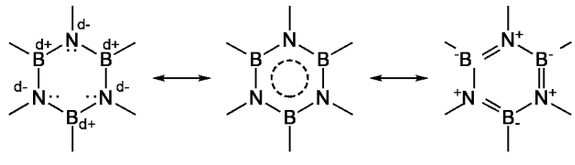
Transformations to the cyclotrimeric borazines and cyclotetrameric tetraza-2,4,6,8,1,3,5,7-tetraboracanes also occur. The rate of dimerization for amino iminoboranes has been shown to be stabilized by bulky substituents (76,79,83). This stabilization through dimerization is essentially a [2 + 2] cycloaddition. There are a number of examples of these compounds forming cycloadducts with other unsaturated polar molecules (78). Iminoboranes can add to electron-deficient carbene complexes of titanium such as $(C_5H_5)_2Ti(CH_2)$ *[84601-70-7]* by [2 + 2] cycloaddition, yielding the metallacycle shown in equation 26 (84).



(26)

Borazines

The largest and most extensively studied family of boron–nitrogen compounds is that of the borazines, characterized by a six-membered ring system containing alternating boron and nitrogen atoms. Borazines are tricoordinated, nearly planar, and have B–N bond lengths considerably shorter than single bonds, indicating partial double-bond character. Because borazine is isoelectronic and isostructural with benzene, it has been called inorganic benzene. The physical properties of borazines tend to confirm π-electron delocalization as in benzenes; however, chemical evidence indicates that the reactions of borazines are dominated by polarization of the B–N bonds.



Formal electron counting would suggest that donation of π-electrons from nitrogen to boron would result in a positive charge on nitrogen and a negative charge on boron as in resonance structure C. However a number of studies have shown the opposite is true with partial negative character on nitrogen and partial positive character on boron resulting from electron-withdrawal by nitrogen through the σ-system (85–88).

Several review articles detailing various aspects of borazine chemistry are available (4,89–93), as well as two comprehensive treatises on preparations, reactions, and properties of borazines (94,95).

Synthesis. The parent compound, borazine *[6569-51-3]*, is best prepared by a two-step process involving formation of *B*-trichloroborazine followed by reduction with sodium borohydride. These reactions have been studied in some detail (96).

$$3\ BCl_3 + 3\ NH_4Cl \rightarrow (-BCl-NH-)_3 + 9\ HCl \tag{27}$$

$$(-BCl-NH-)_3 + 3\ NaBH_4 \rightarrow (-BH-BH-)_3 + 3\ NaCl + \tfrac{3}{2}\ B_2H_6 \tag{28}$$

The heating of sodium borohydride with ammonium chloride in high boiling glycol ether gives borazine in 35% yield (97). A commercially feasible method of producing borazine involves decomposing ammonia borane by heating in a high boiling glycol ether solvent (98).

Symmetrically substituted borazines are generally prepared by reaction of amines and boranes (94).

$$3\ BX_3 + 3\ NH_2R \rightarrow (-BX-NR-)_3 + 6\ HX \tag{29}$$

where X = H, halogen, or alkyl; R = H, alkyl, or aryl. *B*-Trihaloborazines are formed, which are useful in preparing *B*-trialkyl or triarylborazines by reaction with Grignard reagents (97). A process for preparing *B*-trichloroborazine *[41265-87-6]*, $B_3Cl_3H_3N_3$, from boron trichloride and excess ammonia has been patented (99). *B*-Trichloro-*N*-trisubstituted borazines can be reduced using sodium borohydride (eq. 30) to *N*-trisubstituted borazines (96).

$$(-BCl-NR-)_3 + 3\ NaBH_4 \rightarrow (-BH-BR-)_3 + \tfrac{3}{2}\ B_2H_6 + 3\ NaCl \tag{33}$$

Substitution reactions of *B*-trichloro-*N*-trialkyl(or triaryl)borazines and alchohols, phenols, or excess amine yield the corresponding borazines (100,94).

N-Trimethoxyborazines are available from reaction of dichloroboranes and *O*-methyl-*N*,*N*-bis(trimethylsilyl)hydroxylamine (eq. 31). The *B*-trichloro-borazines undergo substitution reactions at the B atoms to give *B*-tri(*tert*-butoxy)- or *B*-tri(*tert*-butyl)-*N*-trimethoxyborazines (101)

$$3\ CH_3ON[Si(CH_3)_3]_2 + 3\ Cl_2BX \rightarrow (-BX-NOCH_3-)_3 + 6\ (CH_3)_3SiCl \tag{31}$$

where X = Cl, OCH_3. *N*-Borylated borazines are formed by heating stannylamines with dibromoboranes according to equation 32 (102). *N*-Tri(*tert*-butyl)borazines have been prepared via

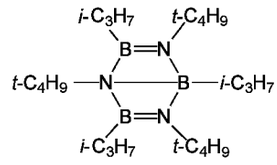
$$3\ R_2B-N(SnR_3)_2 + 3\ RBBr_2 \xrightarrow{\Delta} (-RB-NBR_2-)_3 + 6\ BrSnR_3 \tag{32}$$

trimerization of unstable iminoboranes (103). The sterically crowded *B*-tri(isopropyl)-*N*-tri(*tert*-butyl)borazine, synthesized via equation 33, is the first reported example of a Dewar borazine, which by x-ray crystallography was found to have two short peripheral B–N double bonds (0.136–0.138 nm) and an extra long bridge B–N single bond (0.175 nm).

$$3\ RClB-N(t\text{-}C_4H_9)[Si(CH_3)_3] \xrightarrow[3\ ClSi(CH_3)_3]{\Delta} 3\ [R-B=N\text{-}t\text{-}C_4H_9] \rightarrow (-BR-Nt\text{-}C_4H_9-)_3 \tag{33}$$

As with Dewar benzene, the increased stability of this structure over the planar borazine is thought to result from the extreme interactions of the alkyl

groups (104).



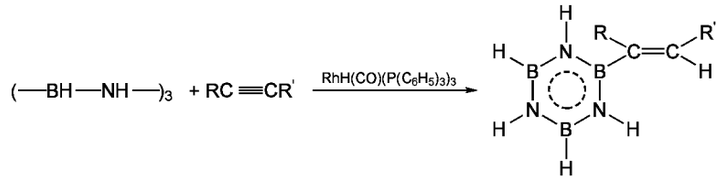
Unsymmetrically *B*-substituted borazines can be prepared by the reaction of *N*-substituted borazines or *B*-trihalogeno-*N*-substituted borazines and the appropriate amount of Grignard reagent (94). Borazines unsymmetrically substituted on nitrogen have been prepared by the reaction of lithium borohydride and ammonium chloride and alkylammonium chlorides (105,106), and by lithiation of *B*-trimethylborazine followed by reaction with alkyl halides (107).

Properties and Reactions. Borazines are liquids or crystalline solids depending on the substitution pattern. Most are sensitive to moisture and must be handled in an inert atmosphere. Borazines are essentially planar except in hexasubstituted cases where there may be some puckering of the borazine ring. A great deal of effort has gone into trying to understand the nature of aromaticity in the borazine ring vis-a-vis benzene. Borazines undergo addition reactions rather than electrophilic substitution reactions typical of benzene compounds. The direction of addition suggests the importance of the polar resonance structure A, ie, Lewis acids add to the ring nitrogen atoms and Lewis bases add to boron atoms. Structural determinations all indicate a planar structure with D_{3h} symmetry (91), and spectroscopic data are consistent with delocalized π-electrons and a bond order greater than 1 (91,108–111). A detailed comparison of spectral data concluded that borazine has a delocalized π-electron system like that of benzene (112); other workers, however, have concluded from spin-coupled calculations that borazine has little aromatic stabilization as compared to benzene (113).

It has been shown that aromatic rings of *B*-triaryl-*N*-triaryl substituted rings are orientated perpendicular to the plane of the borazine ring (114,115). If the aryl rings are substituted it is possible to obtain mixtures of cis and trans isomers (atropisomerism) in which the aryl substituents are on the same or opposite sides of the plane of the borazine ring, respectively (115).

Thermal Stability. Borazine itself shows negligible decomposition at 0–5°C. At ambient temperature 1–2% decomposition has been observed during the first month followed by an increase in rate thereafter, and at higher temperatures appreciable decomposition occurs (89). There has been much interest in utilizing borazine or derivatives as precursors to boron nitride which has the same stoichiometric boron–nitrogen ratio and a hexagonal structure. Yields of boron nitride by ordinary thermolysis of borazine are very low because borazine is a volatile compound. Thermolysis of borazine at 250–700°C under 100 MPa (145,000 psi) pressure produced amorphous boron nitride in good yield (116). The latter compound was converted to cubic boron nitride by much higher temperature and pressure treatment in the presence of cubic B–N seed (117). Cross-linking of borazines through amino groups has produced preceramic polymers, which form hexagonal boron nitride on heating (118). The polymeric compositions can be shaped to form coatings and fibers that yield the corresponding boron nitride-shaped articles on pyrolysis (119).

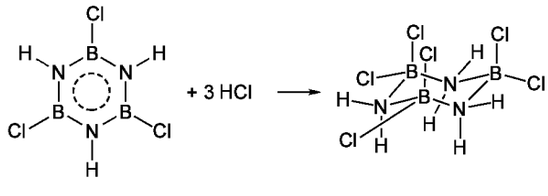
Heating borazine *in vacuo* at 70°C yields poly(borazylene) polymers, which are soluble in solvents such as tetrahydrofuran or glyme and could be thermolyzed to boron nitride in good yields (120). Other soluble preceramic polymers were produced by transition-metal catalyzed formation of *B*-alkenylborazines (eq. 34) which were thermally polymerized under mild conditions to poly(alkenylborazines). The latter yielded boron nitride having low carbon contents when thermolyzed in an ammonia atmosphere (121).



(34)

Hydrolysis. Borazine is slowly hydrolyzed by water at ambient or higher temperatures to boric acid. Substituted borazines react with water to give ring-cleavage products, eg, boronic acids and amines (122). *B*-Trichloroborazine reacts with water to give boric acid and chloramine (123).

Addition Reactions. In general, polar molecules such as hydrogen halides add across the B–N bonds, the more electronegative group bonding to boron (91). The adducts are cyclotriborazanes such as the product formed by reaction of *B*-trichloroborazine and hydrogen chloride (eq. 35). X-ray crystal analysis shows the structure exists in a chair conformation (124).



(35)

Substitution Reactions. Substitution reactions on borazines are confined mainly to substitution by nucleophilic groups on boron; substituents on nitrogen are inert to most reagents. Treatment of *B*-halo or *B*-hydridoborazines with organolithium or Grignard reagents results in substitution at boron with the organic moiety (91,125). Indirect substitution of nitrogen on *B*-trimethylborazine has been effected by formation of the intermediate *N*-trilithioborazine followed by alkylation (107).

Miscellaneous Reactions.

Photolysis. Borazine absorbs strongly in the ultraviolet region between 170–200 nm. Irradiation of borazine in the gas phase with ammonia, water, alcohols, and D_2 produces *B*-monosubstituted derivatives (126–128). From quantum yield studies of the deuterium exchange reaction it was concluded that the exchange proceeds via formation of an excited borazine molecule (128). Photolysis of gaseous borazine itself produced borazanaphthalene and other condensed products (129). Photosensitization of alkylborazines in the presence of hydrogen resulted in dimers formed by joining at the alkyl groups (130).

Complex Formation. *B*-Trichloroborazine was reported to readily form crystalline adducts of uncertain structure with pyridine (131). The Lewis acids aluminum tribromide or gallium trichloride form 1:1 adducts with hexamethylborazine (eq. 36) in which the metal atom coordinates with a nitrogen with loss of planarity of the ring (132,133).

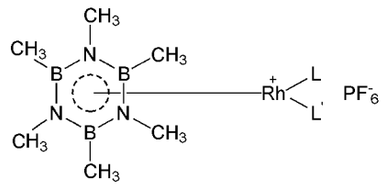
$$(-BCH_3-NCH_3-)_3 + MX_3 \rightarrow (-BCH_3-NCH_3)_3 \cdot MX_3 \qquad (36)$$

where M = Al, X = Br or M = Ga, X = Cl. π-Complexes are formed from hexaalkylborazines and transition metals as in equation 37 (134,135).

$$(-BR-BR-)_3 + (CH_3CN)_3Cr(CO)_3 \rightarrow (-BR-BN-)_3Cr(CO)_3 + 3\,CH_3CN \qquad (37)$$

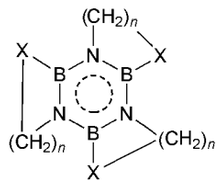
Although isostructural with hexaalkylbenzene metal π-complexes, the borazine complexes are less stable than the benzene analogues, and spectroscopic

evidence suggests that the borazine rings are poorer π-acceptor ligands (135). Cationic-mixed ligand rhodium complexes have been formed with hexamethylborazine. The borazine is easily displaced by σ- or π-donor ligands such as acetonitrile or benzene (136).



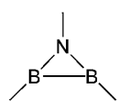
where LL' = diolefin or L = L' = ethylene or CO

Fused Rings and Polymers. Borazine analogues of naphthalene and substituted phenalenes are known; the latter compound is formed by reaction of distannylamine and a large excess of tris(methylthio)borane (137). A general method for the preparation of the polycyclic borazines using fused carbon–heteroatom rings, where X = O, NR and *n* 2, 3, has been given (137).

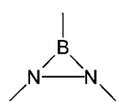


The preparation of a variety of other fused-ring borazine derivatives has been reviewed (95). Oligomers and polymers have been formed in which the borazine rings are linked directly by B–N bonds and where the rings are bridged by *O, N,* or organo groups (91). Borazines linked by urea groups have been prepared as possible preceramic oligomers (138).

Other B–N Ring Systems. A number of unusual ring systems containing only B–N linkages have been reported (139). Derivatives of both possible three-membered ring systems, azadiboradine (1) and diazaboridine (2) have been prepared and the geometries and stabilization energies of these systems calculated (140–142).

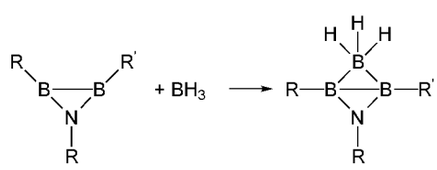


(1)



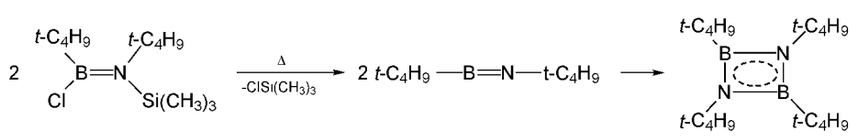
(2)

Unexpectedly the Lewis acid BH_3 was found to add across the B–B bond of azadiboridines rather than to the *N*-atom to give the *nido*-1-azatetraboranes as in equation 38 (143) where R R′ *t*-C_4H_9, and R *t*-C^4H^9, R′ *i*-C_3H_7.



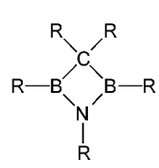
(38)

The four-membered diazadiboretidine ring system has been formed by several routes including replacement of Sn with B in diazadistannetidines (144), thermolysis of diarylazidoboranes (145), reductive elimination of S from six-membered 1,4-dithia-2,6-diaza-3,5-diborinane rings (146), and generally by dimerization of iminoboranes, which are intermediates formed by thermal elimination of chlorotrimethylsilane from aminoboranes as in equation 39 (147,148). Diazadiboretidines act as 4-electron donors forming chromium and tungsten tetracarbonyl complexes (149).

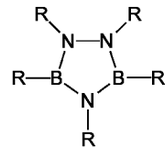


(39)

The four-membered azadiboretidine (3) ring-system has been reported (150,151). Examples of larger B–N ring systems are triazadiborolidines (4) (150), tetraazaborolines (5) (151,152), tetraazadiborines (6) (153), and tetraazatetraborocanes (7) (139,154). The incorporation of B–N linkages into carbocyclic systems has been reviewed (4,154).



(3)



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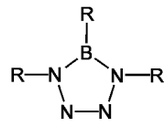

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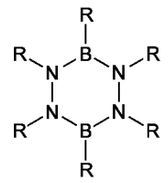

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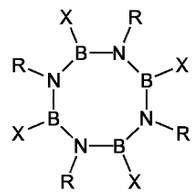
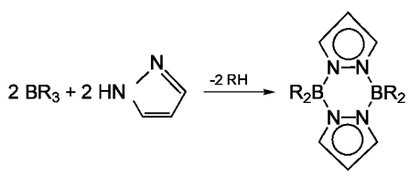


(7)

Of commercial interest are benzo- and other fused aromatic 1,2,3-diazaborine derivatives which have exhibited good antibacterial activity against a variety of microorganisms (155–157). The reaction of pyrazole or *C*-substituted pyrazoles with boranes yields the pyrazabole system, a class of exceptionally stable compounds. More than 70 species in this system have been reported and the subject comprehensively reviewed (158). These compounds have been used as ligands in transition-metal complexes (159).



(40)

Manufacture and Uses

Organic boron–nitrogen compounds have not found extensive usage, and therefore, very few are manufactured on a large scale. Callery Chemical Co. appears to be the largest manufacturer of amine boranes and borazines. Research quantities of some compounds are available from Callery, Aldrich Chemical Co., Alfa, Strem Chemicals, Atomergic, K & K, and Eagle-Picher.

Amine boranes are principally used as reducing agents in inorganic and organic synthesis and in the metal plating industry (see ELECTROLESS PLATING). Boron analogues of amino acids and peptides have antitumor and hypolipidemic activities and are offered for development by Boron Biologicals, Inc. (see CHEMOTHERAPEUTICS, ANTICANCER).

Borazines, particularly polymeric compounds, have been extensively investigated as preceramic materials from which coatings and fibers of boron nitride can be produced upon thermolysis. *B*-aryl and halogeno-amino borazines are reported to have use as fire retardants in cotton and nylon textiles. Other reported uses for borazines are as epoxy resin catalysts, polymerization inhibitors of unsaturated alcohols and esters, and catalysts for polymerization of alkenes (95).

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BOUNDARY LAYER.

See FILM DEPOSITION TECHNIQUES; FLUID MECHANICS.

BRAKE FLUIDS.

See HYDRAULIC FLUIDS.

BRAKE LININGS AND CLUTCH FACINGS

Brake linings and clutch facings consist of friction materials. Friction materials technology encompasses friction material types, their applications, friction and wear characteristics, raw materials, manufacturing methods, and evaluation and test methods.

Brakes. During a stop, a brake converts the kinetic energy of the moving vehicle or machine part into heat, absorbs the heat, and gradually dissipates it into the atmosphere. A brake is a sliding friction couple consisting of a rotor (disk or drum) connected to the wheel or machine and a stator on which is mounted the friction material. The friction material is considered to be the expendable portion of the brake couple which, over a long period of use, is converted to wear debris and gases (1).

Clutches. During engagement a clutch transfers the kinetic energy of a rotating crankshaft (coupled to a power source) to the transmission and wheels. Any slippage results in the generation of heat, which is absorbed and eventually dissipated to the atmosphere by the clutch. Thus the clutch is basically a static friction couple that momentarily slides during gear shifts or other engagements. The clutch friction material facing is considered to be expendable.

Brakes and clutches operate both dry and wet. In dry friction couples, the heat is removed by conduction to the surrounding air and structural members. Wet friction couples operate within a fluid, usually an oil, which absorbs the heat and maintains the couple at relatively low (below 200°C) temperatures. The fluid also traps the wear debris.

Requirements. Automotive brakes must satisfy a certain set of consumer expectations, which includes safety, comfort, durability, and reasonable cost. In technical terms, these expectations are translated into a set of specific requirements such as high and stable friction, no or minimal vibration and noise, and low wear rates for the friction material and rotor mating surfaces, all of which have to be achieved simultaneously at a reasonable cost. Particularly, the performance has to be stable under varying application conditions over extremes in temperature, humidity, speed, and deceleration rate for occasional or many consecutive stops. The requirements for use in machines are less stringent.

The preferred descriptive terms for brake or clutch friction materials according to usage are brake pads, used in disk brakes; brake linings, used in drum brakes; brake segments, used in medium truck drum brakes; brake blocks, used in large truck drum brakes; and brake disks, used in large aircraft brakes. Friction materials for clutches are called facings.

Usage. Friction materials serve in a variety of ways to control the acceleration and deceleration of vehicles and machines. Materials may be as small as a clutch in a business machine or a brake on a bicycle to as large as jumbo aircraft brakes. The brakes on bicycles may have friction couples of iron sliding against iron in the coaster brake, or rubber-bound composite pads sliding against a steel or aluminum wheel rim in hand-activated brakes. Passenger cars may have disk brakes or drum brakes exclusively, or a combination of disk fronts and drum rears (2). The friction materials may be resin- or rubber-bound composites based on asbestos, metallic fibers, or a combination of other fibers. Trucks and off-highway vehicles usually have very large drum brakes; only a few have front disk brakes. These friction couples usually operate at higher friction levels and temperatures than those of passenger cars. Large aircraft are equipped exclusively with disk brakes that contain multiple rotor and stator arrangements having the most popular friction couple consisting of a sintered friction material sliding against a high temperature resistant steel. The newer aircraft brakes consist of carbon composites serving as both the rotor and the stator.

Types of Friction Materials

Prior to the mid-1970s, the most common type of friction materials in use in brakes and clutches for normal duty for original equipment installations and for the aftermarket were termed organics. These materials usually contained about 30–40 wt % of organic components and were asbestos-based (3).

After the mid-1970s, the downsizing of North American vehicles and the introduction of front wheel drive vehicles brought about the widespread usage of a new class of friction materials (4) called semimetallics, also called semimets and carbon–metallics. Because of the allegedly adverse health effects associated with asbestos *[1332-21-4]* (qv) fibers, a second new class of friction materials called nonasbestos organics (NAOs) came about (5). Such materials are called either asbestos-free or nonasbestos friction materials (2).

Asbestos-Based Organic Materials. The primary applications of asbestos-based organic frictional materials and their requirements are *(1)* primary drum brake linings providing high and stable friction at all temperatures and pressures; *(2)* secondary and nonservo drum brake linings providing stable friction and wear resistance; *(3)* Class A disk pads providing friction levels of 0.35–0.45, nonabrasive wear properties, quiet operation, and rotor compatibility; *(4)* Class B disk pads providing higher (0.45–0.60) friction and high temperature wear resistance at the expense of some low temperature wear resistance, noise properties, and rotor compatibility; *(5)* Class C friction materials consisting of both disk pads and block-type friction materials for extremely heavy-duty operations providing high (>0.50) friction and minimal fade at the expense of other brake characteristics such as wear resistance, rotor compatibility, and noise properties; and *(6)* clutch friction materials providing stable friction, good wear properties, quiet operation, and rotor compatibility combined with high strength properties. Class A friction materials were more common on vehicles built in North America; Class Bs were common in Europe and Asia.

The primary constituent of practically all asbestos–organic friction materials was asbestos fiber, with small quantities of other fibrous reinforcement material. Asbestos was chosen because of its thermal stability, its relatively high friction, and its reinforcing properties. Because asbestos alone did not offer all of the desired properties, other materials called property modifiers were added to provide desired levels of friction, wear, fade, recovery, noise, and rotor compatibility. A resin binder held the other materials together. This binder is not completely neutral and makes contributions to the friction and wear characteristics of the composite. The more commonly used ingredients can be found in various patents (6–9).

Nonasbestos Organics. NAOs came about because the replacement of asbestos became desirable and necessary. The 30–70 wt % asbestos in different formulations is replaced by other reinforcements, usually other fibers or other reinforcing materials plus property modifying ingredients. In all cases, the large amount of asbestos was replaced with smaller amounts of nonasbestos fibers, not only because of the processing differences, but because no single alternative fiber can replace asbestos for performance (5). Fiber combinations may be glassy: E-glass or synthetic mineral fiber (SMF) blown from slag; ceramic; metallic: steel, copper, or brass; wollastonite *[14567-51-2]*; or organic: cotton (qv), acrylic, polyaromatics, or cellulose-based (10). The

nonfibrous reinforcers include various platy minerals such as mica *[12001-26-2]* and metallics such as porous metallic powders.

The NAOs found their niche slowly in the 1980s gradually replacing asbestos-based materials and some of the semimetallic front disk pads on U.S. vehicles.

Semimetallic Materials. Semimetallics, also called carbon-metallics, were introduced in the late 1960s but gained widespread usage in the mid-1970s, eventually taking more than 90% of the U.S. passenger car and light truck front axle business in the 1980s. These materials usually contain more than 50 wt % iron and or steel components. They are primarily used as disk pads and blocks for heavy-duty operation.

Initially, the primary constituent of practically all semimetallics was iron powder in conjunction with a small amount of steel fiber (type I) (11). Later, large amounts of steel fiber were used along with small amounts of iron powder (type II). Various property modifiers, eg, ceramic powders, organic or rubber particles, and graphite powders, are added to enhance performance to desired levels, and a resin binder, which is necessary to hold the materials together in a mass, is also added (11). Compared to asbestos-based Class B organics that semimetallics originally replaced, semimetallics offered stable friction, improved fade resistance and durability, rotor compatibility, and quiet operation.

Sintered Materials or Cermets. Heavy weights and high landing speeds of modern aircraft or high speed trains require friction materials that are extremely stable thermally. Organic or semimetallic friction materials are frequently unsatisfactory for these applications. Cermet friction materials are metal-bonded ceramic compositions (see COMPOSITE MATERIALS) (12–14). The metal matrix may be copper or iron (15).

Carbon Composites. Cermet friction materials tend to be heavy, thus making the brake system less energy-efficient. Compared with cermets, carbon (or graphite) is a thermally stable material of low density and reasonably high specific heat. A combination of these properties makes carbon attractive as a brake material and several companies are manufacturing carbon fiber–reinforced carbon-matrix composites, which are used primarily for aircraft brakes and race cars (16). Carbon composites usually consist of three types of carbon: carbon in the fibrous form (see CARBON FIBERS), carbon resulting from the controlled pyrolysis of the resin (usually phenolic-based), and carbon from chemical vapor deposition (CVD) filling the pores (16).

Disk and Drum Materials. Gray cast iron is of reasonably low cost, provides good wear resistance and damping characteristics, and has long been in use as a brake drum or disk material for passenger cars and trucks. Copper or aluminum rotors have been evaluated experimentally (17–19) and alloy steel rotors are being used for certain nonautomotive brakes, including aircraft and trains. Dual structure composite rotors made with gray iron rubbing surfaces cast with steel hubs as stronger, lighter-weight rotors experienced noise and corrosion difficulties.

Developments in metal-matrix composites technology has resulted in aluminum matrix materials filled with silicon carbide *[409-21-2]*, SiC, (see CARBIDES, SILICON CARBIDE) particles (15 to 60 vol %) that provide the possibility of weight reduction for brakes (20). These composite materials are being tested and evaluated.

Friction and Wear

Friction. An analysis of friction mechanisms suggests that a frictional force is likely to consist of several components such as adhesion-tearing, ploughing (or abrasion), elastic and plastic deformation, fracture, shearing of a friction film (glaze) (21), and asperity interlocking, all occurring at the sliding surface. Relative contributions of these mechanisms presumably depend on the normal load and sliding speed as well as the temperature. (Material properties are known to depend on these variables). In the case of automotive friction materials, the coefficient of friction is usually found to decrease with increasing unit pressure and sliding speed at a given temperature, contrary to Amontons' law (22–24). This decrease in friction is controlled by the composition and microstructure of friction materials.

As the temperature of the sliding interface increases, the coefficient of friction varies. This variation is unpredictable, and there exists no general trend except that at extremely high temperatures the coefficient may become very low (<0.15). This temporary loss in friction is referred to as fade (25). Like automotive friction materials, aircraft cermet friction materials exhibit decreasing coefficient of friction with increasing unit pressure (12).

Effectiveness, essentially a measure of the stopping efficiency, can be expressed in a number of different ways: as the coefficient of friction, deceleration rate, hydraulic or air line pressure required, torque developed, or distance required to stop a vehicle. Effectiveness levels used by consumers are typically decelerations of 0.15 to 0.30 *G* achieved at line pressures of 1.2 to 2.5 MPa (12 to 25 bars) in normal braking, increasing up to 0.50 to 0.80 *G* in panic situations requiring 5.5 to 11.0 MPa (55 to 110 bars). The various temperatures are identified for passenger cars as cold (under 100°C), normal (150–250°C), or hot (above 300°C). Effectiveness can be measured new or off-rack (without any prior use), preburnished (after little prior use), burnished (after moderate use), and faded (after use at elevated temperatures). Although the same terms are used for all friction materials, for large aircraft materials the temperatures are cold, under 300°C; normal, 400–600°C; and hot, above 700°C. The normal fade-free maximum operating temperatures of various friction materials may be summarized as drum linings and clutch friction materials, 250°C; Class A organic disk pads, 300°C; Class B organic materials and blocks, 350°C; semimetallics, 400°C; and cermets and carbon composites, 700°C.

Friction peaking is an increase in friction known to occur during or after prior high temperature operation. Imbalance occurs when friction peaking or fade causes one wheel or axle to change in friction, yielding side-to-side or front-to-rear imbalance. Friction stability is the ability of the friction materials to produce similar friction or friction changes at all wheels through all duty cycles and especially during a return to normal operation after a temporary severe duty. Recovery from fade is the ability of the friction material to return to its prefade friction level. Speed sensitivity is the ability to maintain effectiveness at varying surface or rubbing speeds. Most materials show losses in effectiveness at higher speeds with semimetallics being the notable exception. Load insensitivity is the ability to maintain effectiveness at various weight loadings. The ability of a friction material to recover from loss in effectiveness as a result of exposure to water is called water recovery.

Wear. For a fixed amount of braking the amount of wear of automotive friction materials tends to remain fairly constant or increase slightly with respect to brake temperature, but once the brake rotor temperature reaches >200°C, the wear of resin-bonded materials increases exponentially with increasing temperature (26–29). This exponential wear is because of thermal degradation of organic components and other chemical changes. At low temperatures the practically constant wear rate is primarily controlled by abrasion, adhesion, and fatigue (30,31).

When a friction material slides against a rotor, microstructural changes take place on the sliding surfaces of both the friction material and the rotor. The degree of these changes depends on the severity of the sliding conditions: the normal load, the sliding speed, the interface temperature, and the environment. The sliding action generates wear particles from the surfaces, compacts them into a layer, and shears the layer at the same time. This shear layer, either on the friction material or on the rotor, is called a friction film or glaze (or transfer film) (21). The mechanisms involved in wear particle generation are believed to be abrasion, fatigue, fracture, adhesion, and thermal degradation.

The wear, W, of friction materials can best be described by the wear equation (32,33): $W = K P^a V^b t^c$ where K is the wear coefficient, P the normal load, V the sliding speed, t the sliding time, and $a,b,$ and c are a set of parameters for a given friction material–rotor pair at a given temperature.

Wear is an economic consideration. Wear resistance generally, but not always, is inversely related to friction level and other desirable performance characteristics within any class of friction material. The objective is to provide the highest level of wear resistance in the normal use temperature range, a controlled moderate increase at elevated temperatures, and a return to the original lower wear rate when temperatures again return to normal. Contrary to common belief, maximum wear life does not require maximum physical and mechanical properties.

Asbestos-based and NAOs have wear parity within their classes. At low temperatures, Class A organic materials and semimetallic materials wear at a substantially lower rate than Class B organic materials. At extremely high temperatures, the wear rate of Class B organic materials is the best, that of semimetallics in next-best, and that of the Class A organics materials is worst. In the intermediate range, semimetallics are the best, followed by the Class B organic materials. Semimetallics tend to have a high initial or break-in wear rate, which usually becomes lower after conditioning at intermediate temperatures.

Cermet or carbon friction materials operate at substantially higher temperatures than the normal automotive or truck materials. Still the wear rates of these materials increase with the brake temperature. One unique feature of these materials is the formation of a glazed friction film at high temperatures that reduces the wear rate and stabilizes the friction level. Without this glazed layer the wear rate is usually very high.

Raw Materials

Binders. In selecting a resin binder system the processing characteristics must be considered along with the frictional and physical properties. Two types of systems are used. In wet processing, the binder is a viscous liquid, usually a resole or a solution, having characteristics suited to thermoplastic processing techniques. In dry processing, the binder is a powdered material, usually a novolak, that is mixed directly with the other materials; it does not cross-link until heat and pressure are applied. In carbon–carbon composites, resin solution is coated onto graphite fiber and dried before being preformed.

Synthetic resins, such as phenolic and cresylic resins (see PHENOLIC RESINS), are the most commonly used friction material binders, and are usually modified with drying oils, elastomer, cardanol *[37330-39-5]*, an epoxy, phosphorus- or boron-based compounds, or even combinations of two. They are prepared by the addition of the appropriate phenol and formaldehyde *[50-00-0]* in the presence of an acidic or basic catalyst. Polymerization takes place at elevated temperatures. Other resin systems are based on elastomers (see ELASTOMERS, SYNTHETIC), drying oils, or combinations of the above or other polymers.

Metals such as copper, iron, or a combination of the two, usually modified with tin, bismuth, and or lead are used as binders of sintered friction materials where deformation under the high forming pressure is required to lock together the property modifiers within a matrix. Metals such as copper, iron, zinc, aluminum, and occasionally lead are also used as friction modifiers.

Fibrous Reinforcements. The asbestos usually used in friction materials is chrysotile *[12001-29-5]*, $3MgO \cdot 2SiO_2 \cdot 2H_2O$, the principal mineral of the serpentine group (34). Long fiber asbestos, eg, Grade 5, is generally used when dry processing techniques are employed in manufacturing. Shorter fiber asbestos, eg, Grade 7, is used for wet processing techniques. The two grades differ considerably in length of fiber, bulk, absorptiveness, cost, and reinforcing value. Longer fibers permit the bending of secondary linings from flat blanks to curved segments.

Steel, copper, and brass fiber may have a variety of aspect ratios, shape, ie, straight versus curved fibers and cross-sectional geometry, surface roughness, and chemical compositions. Fibers having tight specifications in terms of cleanliness, chemical composition, and aspect ratio are necessary. The fibers are usually machined from larger metallic forms.

Glass fibers and glassy fibers such as SMF or ceramic fibers are generally more thermally resistant than asbestos. The primary criterion for asbestos substitutes is suitable performance and processing characteristics and that they do not become harmful. The E-glass fibers are made by drawing molten glass through noble metal mandrils. SMF is blown from molten slag. Wollastonite is mined and ground into usable forms.

Several types of organic fibers are used: the cellulose-based include cotton (linters), solkafloc, paper (qv), sisal, and other natural fibers; synthetics include acrylics and polyaromatics. Unique are the acrylic and polyaromatic pulps made by microcutting the surfaces of softened fibers. The high surface and charge effects impart processability as well as low temperature reinforcement properties at the expense of higher costs. Carbon–graphite fibers are produced by carbonization–graphitization of organic or pitch fibers by techniques that provide parallel alignment of the carbon chain to the fiber length for maximum tensile strength.

Organic clutch materials contain continuous-strand reinforcements in addition to fibrous reinforcements. These include cotton (primarily for processing), other organic yarns, carbon–graphite yarn, and asbestos yarn, and brass wire or copper wire for high burst strength.

Nonfibrous Reinforcements. Because of the higher costs associated with nonasbestos fibers and the performance requirements needed in replacing asbestos, platy minerals such as mica and talc, and metal powders such as iron and copper, are being used as a portion of the total reinforcement package in NAOs.

Property Modifiers. Property modifiers can, in general, be divided into two classes: nonabrasive and abrasive, and the nonabrasive modifiers can be further classified as high friction or low friction. The most frequently used nonabrasive modifier is a cured resinous friction dust derived from cashew nutshell liquid (see NUTS). Ground rubber is used in particle sizes similar to or slightly coarser than those of the cashew friction dusts for noise, wear, and abrasion control. Carbon black (qv), petroleum coke flour, natural and synthetic graphite, or other carbonaceous materials (see CARBON) are used to control the friction and improve wear, when abrasives are used, or to reduce noise. The above mentioned modifiers are primarily used in organic and semimetallic materials, except for graphite which is used in all friction materials.

Abrasive modifiers are used in several types of friction materials. Very hard materials such as alumina, silicon carbide, and kyanite *[1302-76-7]* are used in fine particle sizes in organic, semimetallic, and cermet materials that are generally less than 74 μm (200 mesh). Particle size is limited by the fact that large particles of such hard materials would groove cast-iron mating surfaces. Larger particle sizes are possible for harder mating surfaces in the special steel rotors used with sintered materials.

Minerals are generally added to improve wear resistance at minimum cost. The most commonly used are ground limestone (whiting) and barytes, though various types of clay, finely divided silicas, and other inexpensive or abundant inorganic materials may also perform this function.

Metal or metal oxides may be added to perform specific functions. Brass chips and copper powder are frequently used in heavy-duty organics where these metallics act as scavengers to break up undesirable surface films. Zinc chips used in Class A organics contribute significantly to recovery of normal performance following fade. Aluminum is also used. Most of these inorganic materials tend to detract from antinoise properties and mating surface compatibility.

Solid lubricants are added to help control high friction characteristics in high speed or heavy-duty applications where high temperatures are generated. Molybdenum disulfide *[1317-33-5]*, MoS_2, may be used alone or in a complex compound formed by grinding with fine natural graphite, and zinc sulfide *[1314-98-3]*, ZnS. Other compounds include calcium fluoride, cryolite *[15096-52-3]*, Na_3AlF , rare-earth oxides, and metal sulfides, eg, iron, antimony, or zinc (see LUBRICATION AND LUBRICANTS).

Manufacturing

An important balance exists between composition that must satisfy performance requirements and ease of manufacture. Various processes employed in the plastics processing industry are used for manufacturing friction materials. Organic linings that must bend also require higher resin contents and longer fibers. Heavy-duty blocks using reduced resin loading for improved performance require molding-to-shape. Sintered and carbon friction materials require high pressure forming and high temperature treatment in inert atmospheres. Woven and some clutch materials require special fiber-forming methods.

The processing of asbestos-based materials has been developed around the unique properties of asbestos, where the fiber bundles open during mixing to entrap the friction modifiers and resin, giving a consistent mix that can easily be compacted. The introduction of NAOs produces a variety of processing problems as the generally stiffer glassy and metallic fibers do not mix or preform as do asbestos-based formulations. The addition of organic pulps, the use of solvent plus drying techniques, or other processing aids are needed for NAOs, especially to control the higher dustiness of basic asbestos-free formulations.

Linings. Most linings are produced from resin wet mix by either an extrusion or a rolling process. Initially, the fibrous reinforcement and the friction modifiers are mixed with a liquid resin at approximately 50°C. The binder solvent serves as a plasticizer to yield a dense puttylike mass having good wet strength. In the extrusion process, the mix is heated to approximately 90°C and extruded at 14–28 MPa (2–4 kpsi) as a flat, pliable tape that is dried for 2 h at 80°C. In the rolling process, the mix is partially dried, sized into particles, then fed between two rolls of slightly different speeds to align the fibers in the flat, pliable tape or green lining that is formed. The green lining is then cut to length, formed into an arcuate segment at 150°C, then placed in curved mold cavities and cured 4–8 h at 180–250°C. Final grinding produces the finished brake lining.

Segments. Segments for heavy-duty use such as for medium-sized trucks are produced by a dry-mix process. The fiber, modifiers, and a dry novolak resin are mixed in an appropriate mixer. The blend is then formed into about a 60 by 90 cm preform (or briquet) at 3–4 MPa (400–600 psi). The briquets are hot-pressed for 3–10 min at 140–160°C and then cooled. The resin is only partially cured at this point to be thermoplastic when subsequently reheated for bending. The hot-pressed preforms are then cut to desired size and bent at 170–190°C and cured in curved molds for 4–8 h at 220–280°C. Final grinding produces the finished segments.

Disk Pads. Organic and semimetallic disks are produced by somewhat similar processes after the mixes are formed. The mix for organics is prepared in an intensive mixer. The mix for semimetallics generally requires a less intensive blender. The mix is then pressed into preforms at room temperature and 28–42 MPa (4–6 kpsi) pressure. These preforms are then hot-pressed at 160–180°C for 5–15 min at 28–55 MPa (4–8 kpsi). Sometimes

the preforms can be eliminated, thus going directly to hot-pressing. The pads are cured at 220–300°C for 4–8 h, and then surface ground to produce the finished disk pads.

In many instances the friction material mix is integrally molded into holes within the backing plate or shoe. Painting of the final assembly, less common in North America, is the rule in Europe and Asia. For controlling brake squeal, noise insulators are widely used. These noise insulating layers are bonded or mechanically attached to the back side of the friction material backing plate.

Blocks. The mix for organic blocks is prepared as for segments and the mix for semimetallic blocks is prepared as for semimetallic disk pads. Preforms are formed at 10–17 MPa (1.5–2.5 kpsi). To reduce blisters in hot-pressing, the preforms may be heated to 90°C for 15–30 min. The blocks are formed at 130–150°C at 14–21 MPa (2–3 kpsi) for periods of 10–30 min. After slitting to width, the blocks undergo grinding of internal and external radii. Final cure may be in an unconfined form at temperatures as low as 180°C for 15 h or in confined form at temperatures as high as 280°C for 6 h. Grinding, drilling, and chamfering produce the final block.

Clutch Materials. Methods for producing most manual clutch friction materials are concerned with the placement of the reinforcement strand or wire within the matrix using some sort of winding operation. Processing includes: molding of mix without strands or wire; molding of mix around strand or wire preforms; or weaving curable preforms. In the first two cases, a dry mix is used. In the latter case, a wet mix is prepared and a strand is run through the premix to pick up the viscous mass along the strand which can be woven after drying. After hot-pressing and curing, the surface is ground to final shape.

For automatic transmissions where the clutch is immersed in oil, paper-based clutch facings are employed. For trucks and heavy off-road equipment, cermet friction materials are also used. Sintered cermet segments are attached to a metal plate to form the clutch facing.

Woven Bands. Woven bands for heavy-duty operation are produced by an expensive process that begins with an asbestos or nonasbestos fiber cord, which may be reinforced with wire, being passed through a wet mix to pick up resin and modifiers. The saturated cord is then woven into tapes that pass through heated rolls to partially cure the resin. The material can be postcured at low temperatures (ca 160°C) to remain as a flexible roll lining or postcured at higher temperature (180–230°C) to form rigid segments. Such materials are used in large band brakes used to control large machinery.

Cermets. Cermet materials are manufactured using the powder metallurgy technique (see METALLURGY, POWDER). Desired amounts of individual ingredients are weighed, mixed, compacted, sintered, and coined or recompacted. The sintering is performed in a reducing or neutral atmosphere, and the sintering temperature has to be high enough so that the metallic ingredients adhere to each other.

Carbon Composites. In this class of materials, carbon or graphite fibers are embedded in a carbon or graphite matrix. The matrix can be formed by two methods: chemical vapor deposition (CVD) and coking. In the case of chemical vapor deposition (see FILM DEPOSITION TECHNIQUES) a hydrocarbon gas is introduced into a reaction chamber in which carbon formed from the decomposition of the gas condenses on the surface of carbon fibers. An alternative method is to mold a carbon fiber–resin mixture into shape and coke the resin precursor at high temperatures and then follow with CVD. In both methods the process has to be repeated until a desired density is obtained.

Evaluation Methods

Chemical, Physical, and Mechanical Tests. Manufactured friction materials are characterized by various chemical, physical, and mechanical tests in addition to friction and wear testing. The chemical tests include thermogravimetric analysis (tga), differential thermal analysis (dta), pyrolysis gas chromatography (pgc), acetone extraction, liquid chromatography (lc), infrared analysis (ir), and x-ray or scanning electron microscope (sem) analysis. Physical and mechanical tests determine properties such as thermal conductivity, specific heat, tensile or flexural strength, and hardness. Much attention has been placed on noise vibration characterization. The use of modal analysis and damping measurements has increased (see NOISE POLLUTION AND ABATEMENT).

Dynamometer and Vehicle Testing. Friction materials are evaluated in the laboratory by a great variety of tests and equipment. Evaluations of friction and wear characteristics using sample dynamometers such as the Chase machine are on the decline. In the most reliable sample test machines the output torque is controlled so that different materials all do the same amount of work. One disadvantage of sample test machines is that the ratios of friction-material area to rotor area and friction-material mass to rotor mass are quite different from the ratios used on vehicles (35). The heat generation, storage, and rejection conditions are therefore quite different, resulting in unreliable data. A second disadvantage is that only one material is tested, whereas in vehicles having drum brakes two types of friction materials may be used together and there are interaction effects. The advantage is mainly one of economics: more tests at less cost.

The full brake dynamometer, when properly instrumented and controlled, reflects the actual brake performance in a vehicle with reasonable accuracy. High initial investment is recovered through operation independent of the climatic conditions and by a fully automatic operation for extended periods, minimizing personnel costs.

Numerous vehicle test procedures are used by different organizations. Performance tests are essentially designed to appraise initial effectiveness, burnish and normal effectiveness, fade and recovery, and final effectiveness. Side-to-side and front-to-rear balance can also be determined. Only vehicle tests can determine noise vibration properties accurately. Wear measurements are generally made in accelerated performance tests, but the results are a reflection of high temperature wear properties and are usually not valid for predicting normal driving wear. More valid predictions of normal wear life result from specifically designed extended road traffic wear measurement tests involving a great number of stops with restricted maximum temperatures.

Vehicle tests are considered the ultimate in friction material evaluation, but to be accurate these tests must be carefully designed to eliminate variations caused by changing conditions. Controlled-temperature tests and parallel-test controlled vehicles normally perform the function satisfactorily but at increased cost.

Environmental and Health Considerations

Manufacturing. Asbestos-based friction materials have been virtually phased out for new vehicle installations because OSHA regulations have limited the exposure of workers to airborne asbestos fibers. High performance friction materials can only be produced by the dry-mix process and this tends to be dustier than other processes. In 1974 the time-weighted average was set by OSHA at 5 fibers cm^3, and reduced in stages as follows: in 1976 reduced to 2.0, in 1986 to 0.2, and in 1990 to 0.1 fibers cm^3. The cost of capital equipment to effect these improvements is extremely high. EPA has passed a ban on asbestos in commerce requiring the complete elimination of asbestos friction materials in phases beginning in 1994. However, the legality of this action has been challenged.

Asbestos and other fibers in a wide variety of bundle sizes or even individual fibrils are in commercial usage. The handling of asbestos and other fibers causes degradation of the larger fiber bundles to fibers having diameters less than two micrometers that remain airborne for extended periods of time. These airborne fibers are prone to inhalation and lung entrapment. The exact definition of harmful fibers and the mechanism by which they affect the body is not accurately known.

Some friction materials may contain other potentially harmful materials. Lead has been found in some secondary linings, Class B and C organic disk pads, and other friction materials as lead metallic particles, oxides, and sulfides. Several original equipment and aftermarket suppliers are known to have a policy against incorporation of lead or other potentially harmful materials in their products.

Wear Products. Friction material and rotor emissions are generated by normal wear. Because of large-scale usage and the potential health hazard of asbestos, asbestos organic friction materials and wear debris have been extensively studied (1,36–38). Below 250°C, abrasive, fatigue, and adhesive wear are considered to be the most important mechanisms and the wear rates are low. Above 250°C, organic friction materials begin to pyrolyze or oxidize such that both gases and particulates are released.

In order to define the extent of emissions from automotive brakes and clutches, a study was carried out in which specially designed wear debris collectors were built for the drum brake, the disk brake, and the clutch of a popular U.S. vehicle (1). The vehicle was driven through various test cycles to determine the extent and type of brake emissions generated under all driving conditions. Typical original equipment and aftermarket friction materials were evaluated. Brake relines were made to simulate consumer practices. The wear debris was analyzed by a combination of optical and electron microscopy to ascertain the asbestos content and its particle size distribution. It was found that more than 99.7% of the asbestos was converted to a nonfibrous form and

that only 3.2% of the total asbestos was emitted to the atmosphere. A second study of brake emissions adjacent to a city freeway exit ramp on the downwind side indicated that the asbestos emissions were so low as not to be distinguished from the background on the upwind side (37).

Future Prospects

The trend began in the 1970s toward more energy-efficient passenger cars and trucks is putting an increased demand on friction materials performance, resulting from smaller and lighter brakes. More efficient vehicles have manual transmissions and smaller brakes. Organic friction materials continue to serve the drum brake industry, but are being replaced by a trend to 4-wheel disk brakes, which are also preferred for antiskid brake systems. As brakes become smaller, producing higher brake temperatures, the Class A NAOs are expected to become less suitable, requiring Class B NAOs. Most recently NAOs having reduced metal contents have started to replace some semimetallics, and "LoMets" and "NoMets" are being explored. Trucks and other heavy vehicles are also moving toward more efficient disk brakes. More sintered friction materials are expected to appear in the heavy-vehicle clutch market. At the same time, aircraft continue to move toward light carbon brakes.

Future brakes must satisfy health standards and most vehicle manufacturers have moved toward removing all asbestos from brakes. Lighter weight rotors and calipers based on aluminum-based metal-matrix materials are also on the horizon for lighter vehicles requiring a whole new family of compatible friction materials.

There is much interest and concern for noise vibration-free brake systems and there is much activity toward friction couples having reduced noise vibration properties. In addition to better noise insulators, brake modifications in the form of different materials, different designs, and improved friction materials formulations and or processes are being developed and implemented.

Economic Aspects

The friction material industry consists of several large organizations having many divisions, as well as more than 60 smaller companies. The primary suppliers' approximate worldwide market share, trade names, and joint ventures licensees (jv l) as of mid-1991 were: Allied-Signal (21%): Bendix, Certified, Jurid, Bendix Europe (Valeo), and Energit with jv l: Bendix-Mintex, Induben, Incolbestos, Varteks, Mex-Para, Kayaba, Hankuk, others; British Belting and Asbestos (BBA) (17%): Mintex, Don, Textar, Fressek, Frenosa, AP, and SBF, with licensees: Bendix-Mintex, Plasbestos, Nisshinbo, others; Turner-Newell (13%): Ferodo, Beral, Nuturn, Belaco, and jv l: JBI; ICI Industries (6%): Abex and jv l: Canparts, Abex, Nisshinbo, and Frendo; General Motors (5%): Delco and Inland with jv l: Ambrake (Akebono), Sumitomo; Echlin (4%): Echlin, Distex, R&D, and licensees: Itapsa, Friction Materials Inc; Japan (17%): Akebono, Nisshinbo, Asahi Asbestos, Hitachi, Japan Brake, others; and others (16%) that individually supply more than 0.4%: Raymark (Raybestos), Carlisle, Friction Products (Thiokol, Brassbestos), Rutgerswerke AG (Pagid, Cobreq, and Hipag), ITT (Galfer), A S Roulands, Thermoid, Wellman, Krasne, Friction Tech, Wu-Tai, Hangzou, Sangshin, and others. Most of those in the United States are registered with the Friction Materials Standards Institute, Paramus, New Jersey.

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BRANDY.

See BEVERAGE SPIRITS, DISTILLED.

BRASS.

See COPPER ALLOYS.

BRAZING ALLOYS.

See SOLDERS AND BRAZING ALLOYS.

BREAD.

See BAKERY PROCESSES AND LEAVENING AGENTS.

BRIGHTENERS, FLUORESCENT.

See FLUORESCENT BRIGHTENERS.

BROMINE

Bromine *[7726-95-6]*, Br_2, is the only nonmetallic element that is a liquid at standard conditions. Bromine *[10097-32-2]*, Br, has at no. 35, at wt 79.904, and belongs to Group 17 (VIIA) of the Periodic Table, the halogens. Its electronic configuration is $1s^2 2s^2 2p\ 3s^2 3p\ 3d^{10} 4s^2 4p^5$. The element's known isotopes range in mass number from 74 to 90. Isotopes usable as radioactive tracers are 77, 80, 80m (metastable), and 82. Bromine has two stable isotopes, ^{79}Br and ^{81}Br. The most common valence states are 1 and +5, but +1, +3, and +7 are also observed. The covalent radius of bromine is 0.1193 nm. The ionic radius of the bromide ion *[24959-67-9]*, Br , is 0.197 nm and of bromine(VII) *[20681-12-3]*, Br^{+7}, is 0.039 nm. The name bromine is derived from the Greek word, *bromos,* meaning stench.

In 1826 Antoine-Jerome Balard in France published the discovery of bromine which was isolated by chlorinating seawater bitterns and distilling out bromine. Bromine had been prepared earlier by Joss and Liebig but neither of them recognized it as an element (1). Bromine was used in photography in about 1840. The first medical use was in 1857 when bromides were used for the treatment of epilepsy. The first commercial bromine production in the United States was in 1846 at Freeport, Pennsylvania. In 1858 potash was discovered in the Stassfurt salt deposits in Germany and bromine was a by-product. Herbert Dow invented the "blowing out" process for Midland (Michigan) brines in 1889. The antiknock properties of tetraethyl lead *[78-00-2]*, $(CH_3CH_2)_4Pb$, were discovered in 1921 and soon after ethylene dibromide *[106-93-4]*, $C_2H_4Br_2$, was found to aid the removal of lead from combustion chambers. At one time about 80% of all bromine was used to produce ethylene dibromide. Bromine was first commercially extracted from seawater in 1934. In the 1950s bromine was discovered in south Arkansas brines, the only significant source of bromine in the United States (see CHEMICALS FROM BRINE).

Physical Properties

Bromine is a dense, dark red, mobile liquid that vaporizes readily at room temperature to give a red vapor that is highly corrosive to many materials and human tissues. Bromine liquid and vapor, up to about 600°C, are diatomic (Br_2). Table 1 summarizes the physical properties of bromine.

Table 1. Physical Properties of Bromine[a]

Property	Value
stable isotope abundance, %	
^{79}Br	50.54%
^{81}Br	49.46%
mol wt	159.808
freezing point, °C	7.25
bp, °C	58.8
density, g mL	
15°C	3.1396
20°C	3.1226
25°C	3.1055
30°C	3.0879
vapor density, g L, 0°C, 101.3 kPa[b]	7.139
refractive index	

20°C	1.6083
25°C	1.6475
viscosity, mm^2/s (cSt)	
20°C	3.14×10^{-1}
30°C	2.88×10^{-1}
40°C	2.64×10^{-1}
50°C	2.45×10^{-1}
surface tension, mN/m (dyn/cm), 25°C	40.9
solubility parameter, 25°C, $(J/cm^3)^{1/2}$ [c]	23.5
critical temperature, °C	311
critical pressure, MPa[d]	10.3
thermal conductivity, W/(m·K)	0.123
specific conductivity, $(\Omega \cdot cm)^{-1}$	9.10×10^{-12}
dielectric constant, 25°C, 10^5 Hz	3.33
electrical resistivity, 25°C, Ω·cm	6.5×10^{10}
expansion coefficient from 20–30°C, per °C	0.0011
compressibility, 20°C from 0–10 MPa[d]	62.5×10^{-6}
heat of vaporization, 50°C, J/g[c]	187
heat of fusion, −7.25°C, J/g[c]	66.11
heat capacity, J/mol[c]	
15 K	7.217
30 K	22.443
60 K	36.33
240 K	57.94
265.9 K	61.64
265.9 K[e]	77.735
288.15 K[f]	78.66
electronegativity	3.0
electron affinity, kJ[c]	330.5

[a] Refs. 2–5.

[b] To convert kPa to mm Hg, multiply by 7.50.

[c] To convert J to cal, divide by 4.184.

[d] To convert MPa to bar, multiply by 10.

[e] Solid bromine.

[f] Liquid bromine.

Bromine is moderately soluble in water, 33.6 g/L at 25°C. It gives a crystalline hydrate having a formula of $\sim Br_2 \cdot 7.9H_2O$ (6). The solubilities of bromine in water at several temperatures are given in Table 2. Aqueous bromine solubility increases in the presence of bromides or chlorides because of complex ion formation. This increase in the presence of bromides is illustrated in Figure 1. Equilibrium constants for the formation of the tribromide and pentabromide ions at 25°C have been reported (11).

$$Br_2 + Br^- \rightleftharpoons Br_3^- \qquad K = 16.85\ M^{-1}$$

$$Br_3^- + Br_2 \rightleftharpoons Br_5^- \qquad K = 1.45\ M^{-1}$$

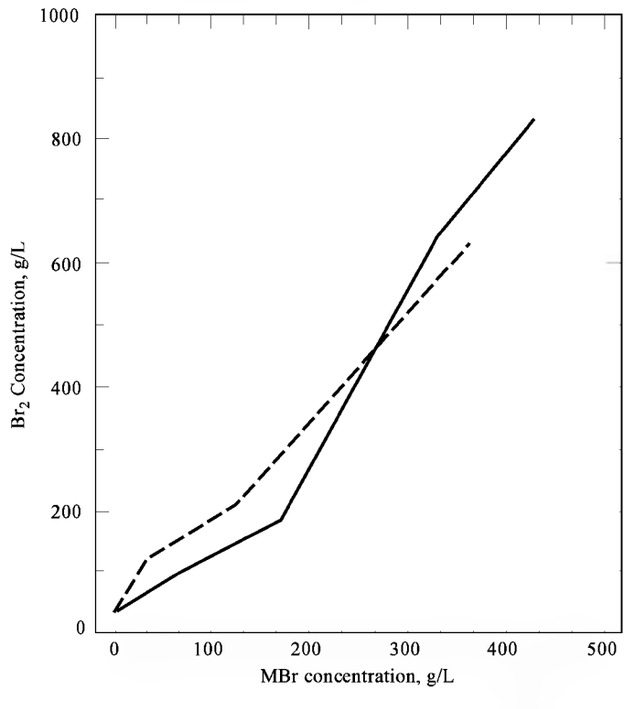


Fig. 1. Solubility of bromine in presence of (—) NaBr and (- - -) KBr (10).

Table 2. Aqueous Solubility of Bromine[a]

Temperature, °C	Solubility, g 100 g soln	Temperature, °C	Solubility, g 100 g soln
0	2.31 (4.05)[b]	20	3.41
3	3.08 (3.85)[b]	25	3.35
5	3.54 (3.77)[b]	40	3.33
10	3.60	53.6[c]	3.50

[a] Refs. 7–9.

[b] These solutions are metastable.

[c] This is the boiling point.

Bromine is soluble in nonpolar solvents and in certain polar solvents such as alcohol and sulfuric acid. It is miscible with alcohol, ether, carbon disulfide, and many halogenated solvents. Bromine reacts with some of these solvents under certain conditions.

Bromine can function as a solvent. One of the very few metal bromides that has significant solubility in bromine is cesium bromide, 19.3 g 100 g of solution, thus providing a method of separating cesium bromide from the other alkali bromides (12). Aluminum bromide also is reported to have significant solubility in bromine but the published solubility values are not in good agreement (13). Bromine serves as the solvent in some brominations of organic compounds, such as 1,2-diphenylethane (14).

Chemical Properties

One of the central features of the chemistry of the halogens is the tendency to acquire an electron to form either a negative ion, X , or a single covalent bond, X, and bromine is no exception. The halogens are electron rich systems having few potential bonding orbitals. Except for helium and neon, all of the elements in the Periodic Table form halides with one or more of the halogens. Halides that are predominately ionic tend to have high conductivities when fused, high boiling points, and if soluble in water, are generally not hydrolyzed. Predominately covalent halides are volatile, nonconductive in the liquid state, and usually readily hydrolyzed (15).

Nonmetal halides are generally hydrolyzed to a hydrogen halide and to an oxy-acid containing the other element. The first row nonmetal halides, eg, CCl_4, resist hydrolysis because the nonmetal element cannot expand its octet of electrons to form a bond to water before its bond to the halide is broken. Hydrolysis requires either an energetic water molecule to strike the halide or ionization of the covalent nonmetal–halide bond, processes that tend to be quite slow (16).

Reaction with Hydrogen and Metals. Bromine combines directly with hydrogen at elevated temperatures and this is the basis for the commercial production of hydrogen bromide *[10036-10-6]*. Heated charcoal and finely divided platinum metals are catalysts for the reaction (17).

Bromine reacts with essentially all metals, except tantalum and niobium, although elevated temperatures are sometimes required, eg, solid sodium does not react with dry bromine but sodium vapor reacts vigorously. Metals such as lead, magnesium, nickel, and silver react with bromine to form a surface coat of bromide that resists further attack. This protective coating allows lead and nickel to be used as linings in bromine containers. Metals tend to be corroded by bromine faster in the presence of moisture than without, probably because of the formation of hydrobromic and hypobromous acids.

Bromine reacts with some metal oxides, eg, thorium oxide, at high temperatures in the presence of reducing agents to form bromides (18). Certain nonhydrated metal halides can be formed by precipitation. These include AgBr, CuBr, AuBr, TlBr, $PbBr_2$, $PtBr_2$, and Hg_2Br_2 (19).

Reaction with Other Halides. Bromide ion is oxidized by chlorine to bromine. This is the basic reaction in the production of bromine from seawater, brines, or bitterns.

$$2\,Br^- + Cl_2 \rightarrow Br_2 + 2\,Cl^-$$

Iodide ion is oxidized by bromine to iodine.

$$2\,I^- + Br_2 \rightarrow I_2 + 2\,Br^-$$

Among the interhalogen compounds containing bromine are BrF, BrF_3, BrF_5, BrCl, and IBr. The interhalogens are characterized by great reactivity. The higher fluorides are quite thermally stable. Bromine pentafluoride *[7789-30-2]*, BrF_5, stable up to 460°C, is the most reactive of the higher fluorides and reacts with all of the elements except nitrogen, oxygen, and the noble gases (15). Solid polyhalide salts are known. Examples are NH_4IBr_2, $RbBrCl_2$, and KClIBr (20).

Reaction with Nonmetals. Bromine oxidizes sulfur and a number of its compounds.

$$H_2S + Br_2 \rightarrow S + 2\,HBr$$

$$S + 3\,Br_2 + 4\,H_2O \rightarrow H_2SO_4 + 6\,HBr$$

$$SO_2 + Br_2 + 2\,H_2O \rightarrow 2\,HBr + H_2SO_4$$

$$Na_2S + 4\,Br_2 + 8\,NaOH \rightarrow Na_2SO_4 + 8\,NaBr + 4\,H_2O$$

Bromine also oxides red phosphorus and some phosphorus compounds.

$$2\,P + 3\,Br_2 + 6\,H_2O \rightarrow 6\,HBr + 2\,H_3PO_3$$

$$H_3PO_3 + Br_2 + H_2O \rightarrow H_3PO_4 + 2\,HBr$$

$$H_3PO_3 + Br_2 + 3\,NaOH \rightarrow NaH_2PO_4 + 2\,NaBr + 2\,H_2O$$

Ammonia, hydrazine, nitrites, and azides are oxidized by bromine. Nitrogen is often a product of such reactions.

$$2\,NH_3 + 3\,Br_2 + 6\,NaOH \rightarrow 6\,NaBr + N_2\uparrow + 6\,H_2O$$

$$8\,NH_4OH + 3\,Br_2 \rightarrow 6\,NH_4Br + N_2\uparrow + 8\,H_2O$$

$$N_2H_4 + 2\,Br_2 + 4\,NaOH \rightarrow 4\,NaBr + N_2\uparrow + 4\,H_2O$$

$$NaNO_2 + Br_2 + H_2O \rightarrow NaNO_3 + 2\,HBr$$

$$2\,NaN_3 + Br_2 \xrightarrow{H_2O} 2\,NaBr + 3\,N_2\uparrow$$

Under certain circumstances bromine reacts with ammonia and amino compounds to form bromamide *[14519-10-9]*, NH_2Br, bromimide *[14519-03-0]*, $NHBr_2$, or nitrogen bromide *[15162-90-0]*, NBr_3. These compounds can decompose explosively so great care should be exercised any time bromine and ammonia or amino compounds might come in contact with each other.

Bromine oxidizes carbon and reacts with carbon monoxide to form carbonyl bromide *[593-95-3]*.

$$C + Br_2 + H_2O \rightarrow 2\,HBr + CO\uparrow$$

$$Br_2 + CO \rightarrow COBr_2$$

Reactions in Water. The ionization potential for bromine is 11.8 eV and the electron affinity is 3.78 eV. The heat of dissociation of the Br_2 molecule is 192 kJ (46 kcal). The reduction potentials for bromine and oxybromide anions in aqueous acid solutions at 25°C are (21):

$$Br_2(aq) + 2\,e \rightarrow 2\,Br \qquad E^\circ = +1.0873\ V$$

$$Br_2(l) + 2\,e \rightarrow 2\,Br \qquad E^\circ = +1.066\ V$$

$$HOBr + H^+ + 2\,e \rightarrow Br^- + H_2O \qquad E^\circ = +1.331\ V$$

$$HOBr + H^+ + e \rightarrow \tfrac{1}{2}\,Br_2(aq) + H_2O \qquad E^\circ = +1.574\ V$$

$$HOBr + H^+ + e^- \rightarrow \tfrac{1}{2}\,Br_2(l) + H_2O \qquad E^\circ = +1.596\ V$$

$$BrO^- + H_2O + 2\,e \rightarrow Br^- + 2\,OH^- \qquad E^\circ = +0.761\ V$$

$$BrO_3^- + 6\,H^+ + 5\,e \rightarrow \tfrac{1}{2}\,Br_2 + 3\,H_2O \qquad E^\circ = +1.482\ V$$

$$BrO_3^- + 6\,H^+ + 6\,e \rightarrow Br^- + 3\,H_2O \qquad E^\circ = +1.423\ V$$

$$BrO_3^- + 3\,H_2O + 6\,e \rightarrow Br^- + 6\,OH^- \qquad E^\circ = +0.61\ V$$

When bromine dissolves in water, it partially disproportionates.

$$Br_2 + H_2O \rightleftharpoons HOBr + H^+ + Br^-$$

The equilibrium constant for this reaction at 25°C is $7.2 \times 10^{-9}\ M^2$ (22). Light catalyzes the decomposition of hypobromous acid to hydrogen bromide and oxygen.

$$HOBr \xrightarrow{h\nu} HBr + \tfrac{1}{2}\,O_2$$

In the dark, hypobromous acid decomposes to bromic acid and bromine. Bromic acid is relatively unstable and decomposes slowly to give bromine and oxygen.

$$5\,HOBr \rightarrow HBrO_3 + 2\,Br_2 + 2\,H_2O$$

$$4\,HBrO_3 \rightarrow 2\,Br_2 + 5\,O_2 + 2\,H_2O$$

In alkaline solution, bromine reacts rapidly to produce hypobromite.

$$Br_2 + 2\,OH^- \rightleftharpoons Br^- + BrO^- + H_2O \qquad K = 2 \times 10^8$$

It is necessary to maintain this reaction below 0°C to minimize the disproportionation of hypobromite to bromate and bromide.

$$3\,BrO^- \rightarrow 2\,Br^- + BrO_3^-$$

Because they are unstable, hypobromites are usually prepared just before use for such jobs as textile bleaching and desizing. In alkaline solutions at 50–80°C bromine reacts to form bromide and bromate. This reaction is reversed in acidic solutions.

$$3\,Br_2 + 6\,OH^- \rightarrow 5\,Br^- + BrO_3^- + 3\,H_2O$$

$$5\,Br^- + BrO_3^- + 6\,H^+ \rightarrow 3\,Br_2 + 3\,H_2O$$

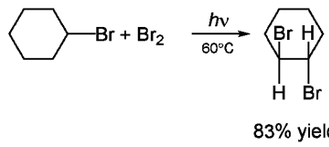
Reactions with Organic Compounds. The addition of bromine to unsaturated carbon compounds occurs readily.

$$CH_2{=}CH_2 + Br_2 \rightarrow BrCH_2CH_2Br$$

Conjugated double bond systems usually undergo 1,4-addition.

$$CH_2{=}CH{-}CH{=}CH_2 + Br_2 \rightarrow BrCH_2CH{=}CHCH_2Br$$

Bromine reacts directly with alkanes but this reaction has little value because mixtures are obtained. However, photochemical bromination of alkyl bromides can be quite selective (23).



83% yield

The bromination of aromatic hydrocarbons can occur either in a side chain or on the ring, depending on conditions. In the presence of sunlight alkylbenzenes are brominated predominately in the side chain (24).

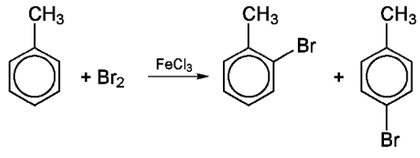
$$Br_2 \xrightarrow{h\nu} 2\,Br\cdot$$

$$Br\cdot + C_6H_5CH_3 \rightarrow C_6H_5CH_2\cdot + HBr$$

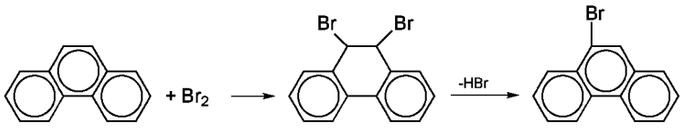
$$C_6H_5CH_2\cdot + Br_2 \rightarrow C_6H_5CH_2Br + Br\cdot$$

$$2\,Br\cdot \rightarrow Br_2$$

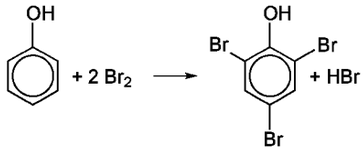
In the presence of halogen Lewis acids, such as metal halides or iodine, aromatic hydrocarbons are halogenated on the ring (24).



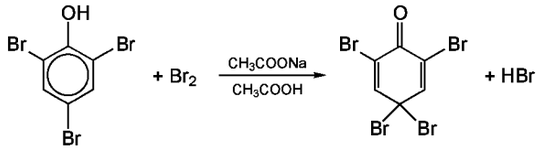
Some polynuclear aromatics, such as anthracene, can be brominated without a catalyst (23).



Phenols and phenol ethers readily undergo mono-, di-, or tribromination in inert solvents depending on the amount of bromine used. In water the main product is the 2,4,6-tribromophenol *[118-79-6]*, $C_6H_3Br_3O$ (23). In water or acetic acid anilines also give the tribrominated product (25).



Tribromophenol can be further brominated in buffered acetic acid to give 2,4,4,6-tetrabromo-2,5-cyclohexadien-1-one *[20244-61-5]*, a useful brominating agent (26).



Heterocyclic compounds range from those, such as furan which is readily halogenated and tends to give polyhalogenated products, to pyridine which forms a complex with aluminum chloride that can only be brominated to 50% reaction (23).

Aliphatic ketones (qv) are readily brominated in the alpha position. Mixtures are usually obtained (24).

$$RCH_2COCH_2R + Br_2 \rightarrow RCHBrCOCH_2R + HBr$$

Bromination of aldehydes (qv) is more complicated because bromination can take place on the aldehyde carbon as well as the α-carbon. Acetals are brominated satisfactorily in cold chloroform solution in the presence of calcium carbonate, which reacts with the hydrogen bromide formed (24).

$$2\,RCH_2CH(OC_2H_5)_2 + 2\,Br_2 + CaCO_3 \rightarrow 2\,RCHBrCH(OC_2H_5)_2 + CaBr_2 + H_2O + CO_2\uparrow$$

Acids and esters (see ESTERS, ORGANIC) are less easily brominated than aldehydes or ketones. Acid chlorides and anhydrides are more easily brominated (23).

$$RCH_2COCl + Br_2 \rightarrow RCHBrCOCl + HBr$$

Bromination of α-chloro ethers proceeds readily and often gives 90–95% yields (24).

$$RCH_2CHClOR' + Br_2 \rightarrow RCHBrCHBrOR' + HCl$$

Bromine can replace sulfonic acid groups on aromatic rings that also contain activating groups. Phenolic sulfonic acids, for example, are polybrominated (24).

$$4\text{-}HOC_6H_4SO_3K + Br_2,\ H_2O \rightarrow 2,4,6\text{-}Br_3C_6H_2OH + KHSO_3$$

Organometallic compounds can react with bromine to give bromides, but because organometallic compounds are frequently made from bromides the reaction with iodine to give iodides is of more synthetic significance (24).

$$RHgX + Br_2 \rightarrow RBr + HgXBr$$

Bromine reacts with the silver salts of carboxylic acids to give an alkyl bromide containing one less carbon atom than the acid (24).

$$RCOOAg + Br_2 \rightarrow RBr + CO_2 + AgBr$$

Amides and imides can be *N*-brominated in the cold by alkali hypobromites (24).

$$RCONH_2 + Br_2 + KOH \rightarrow RCONHBr + KBr + H_2O$$

During some brominations a hydroxyl group can be converted to a ketone on an adjacent carbon atom (27).

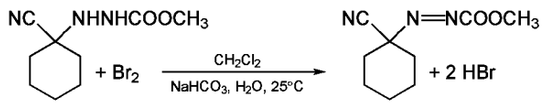
$$(CH_3)_2C(OH)CH_2CH_3 + Br_2 \rightarrow (CH_3)_2CBrCHBrCH_3 + H_2O$$

$$(CH_3)_2CBrCHBrCH_3 + H_2O \rightarrow (CH_3)_2CHCOCH_3 + 2\,HBr$$

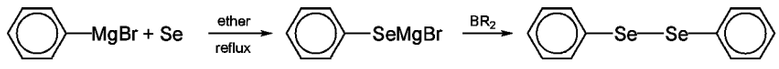
In the presence of base, bromine reacts with acetylenes to displace a hydrogen (28).

$$C_6H_5C{\equiv}CH + Br_2 + NaOH \rightarrow C_6H_5C{\equiv}CBr + NaBr + H_2O$$

Hydrazines can be oxidized by bromine (29).



Bromine has been used to synthesize organoselenium compounds (30).



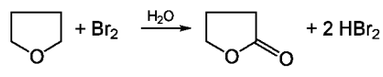
In an aqueous acetate buffer at pH 5 bromine oxidizes ethers containing an α-hydrogen (31).

$$(CH_3CH_2CH_2)_2O + Br_2 \xrightarrow{H_2O} 2\,CH_3CH_2COOH + 2\,HBr$$

ca 100%

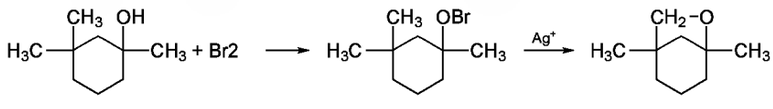
$$(C_6H_5CH_2)_2O + Br_2 \xrightarrow{H_2O} 2\,C_6H_5CHO + 2\,HBr$$

98%

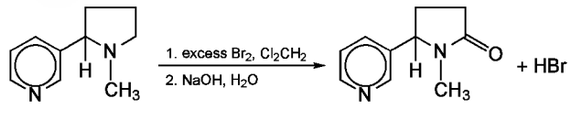


ca 100%

In the presence of a silver salt, bromine reacts with a tertiary alcohol to give a product corresponding to an insertion of oxygen (32).

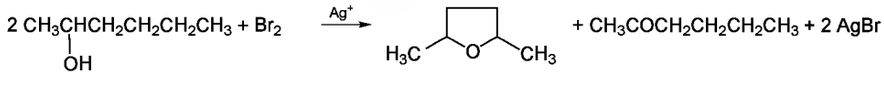


Bromine can oxidize certain tertiary amines to lactams (33).

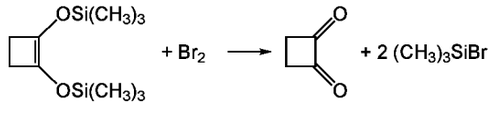


50%

When tertiary alcohols are oxidized with bromine and a silver salt, tetrahydrofuran derivatives result (34).



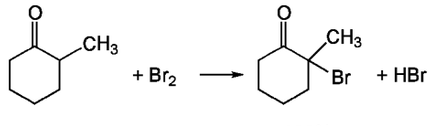
Bromine has been used to form cyclobutane-1,2-dione *[33689-28-0]*, $C_4H_4O_2$, when other methods failed (35,36).



Regioselective bromination of ketones at the more highly substituted α-position is effected by photocatalytic bromination in the presence of 1,2-epoxycyclohexane (37).

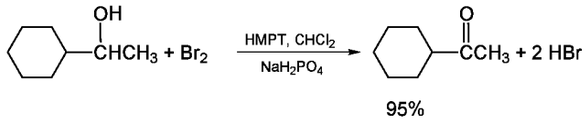
$$CH_3COCH(CH_3)_2 + Br_2 \xrightarrow[\text{1,2 epoxycyclohexane}]{h\nu} CH_3COCBr(CH_3)_2 + HBr$$

100%

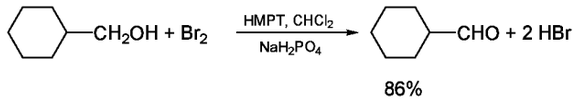


100%

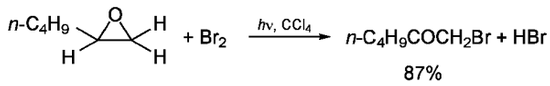
Bromine or chlorine dissolved in hexamethylphosphoric triamide *[680-31-9]* (HMPT) with a base, eg, NaH_2PO_4, present, oxidizes primary and secondary alcohols to carbonyl compounds in high yield (38).

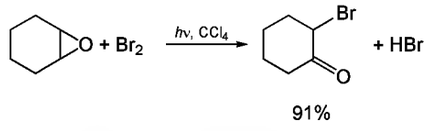


95%

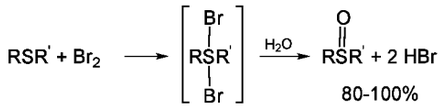


Brominating epoxides in CCl_4 under irradiation gives α-bromo ketones (39).

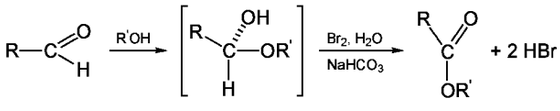




Bromine in a two-phase system, $H_2O–CH_2Cl_2$, with $KHCO_3$ can convert sulfides to sulfoxides in good yields (40).



Aldehydes can be directly converted to esters using bromine in alcohol solvents with sodium bicarbonate buffer (41).



Organic compounds that are easily oxidized are destroyed by bromine.

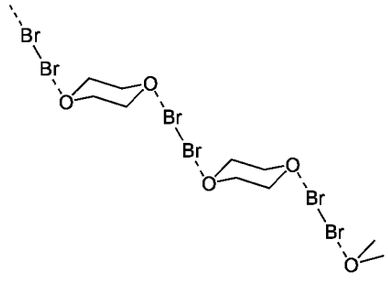
$$HCHO + 2\,Br_2 + 4\,NaOH \rightarrow 4\,NaBr + CO_2\uparrow + 3\,H_2O$$

$$HCOOH + Br_2 \xrightarrow{H_2O} CO_2\uparrow + 2\,HBr$$

$$NH_2CONH_2 + 3\,Br_2 + 6\,NaOH \rightarrow 6\,NaBr + N_2\uparrow + CO_2\uparrow + 5\,H_2O$$

Charge-Transfer Compounds. Similar to iodine and chlorine, bromine can form charge-transfer complexes with organic molecules that can serve as Lewis bases. The frequency of the intense uv charge-transfer adsorption band is dependent on the ionization potential of the donor solvent molecule. Electronic charge can be transferred from a π-electron system as in the case of aromatic compounds or from lone-pairs of electrons as in ethers and amines.

Charge-transfer compounds can be isolated in the crystalline state, although low temperatures are often required. The bromine–dioxane compound, for example, has a chain structure (42).



Occurrence

Bromine is widely distributed in nature but in relatively small amounts. Its abundance in igneous rock is 0.00016% by weight and in seawater is 0.0065% by weight. The only natural minerals that contain bromine are some silver halides, including bromyrite *[14358-95-3]*, AgBr, embolite *[1301-83-3]*, Ag(Cl,Br), and iodobromite, Ag(Cl,Br,I). Sources of commercial bromine are underground brines in Arkansas, which contain 3–5 g/L bromine, and in China, Russia, and the United Kingdom; bitterns from mined potash in France and Germany; seawater or seawater bitterns in France, India, Italy, Japan, and Spain; and bitterns of potash production from Dead Sea brines, which contain 4–6 g/L bromine, in Israel (43).

An average of about 7 ppm of bromine is found in terrestrial plants, and edible foods contain up to 20 ppm. Among animals the highest bromide contents are found in sea life, such as fish, sponges, and crustaceans (44). Animal tissues contain 1–9 ppm of bromide and blood 5–15 ppm. The World Health Organization has set a maximum acceptable bromide intake for humans at 1 mg/kg of body weight per day. In adult males the bromine content in serum has been found to be 3.2–5.6 μg/mL, in urine 0.3–7.0 μg/mL, and in hair 1.1–49.0 μg/mL. Bromine may be an essential trace element as are the other halides (45).

Bromine compounds are found in the atmosphere in small amounts; the sea is a primary source. Rainfall over the Pacific and Indian Oceans has been found to contain 60–80 μg/L of bromine (46). Approximately 10 parts per trillion (v/v) of bromine is found in the stratosphere (47).

Manufacture

Bromine occurs in the form of bromide in seawater and in natural brine deposits (see CHEMICALS FROM BRINE). Chloride is also present. In all current methods of bromine production, chlorine, which has a higher reduction potential than bromine, is used to oxidize bromide to bromine.

$$\tfrac{1}{2}\,Cl_2(g) + e^- \rightarrow Cl^- \qquad E^\circ = +1.356\ V$$

$$\frac{1}{2}\,Br_2(g) + e^- \rightarrow Br^- \qquad E^\circ = +1.065\ V$$

$$2\,Br^- + Cl_2 \rightarrow Br_2 + 2\,Cl^-$$

There are four principal steps in bromine production: (*1*) oxidation of bromide to bromine; (*2*) stripping bromine from the aqueous solution; (*3*) separation of bromine from the vapor; and (*4*) purification of the bromine. Most of the differences between the various bromine manufacturing processes are in the stripping step.

Traditional Processes. The two primary stripping vapors are steam and air. Steam is used when the concentration of bromine in brine is greater than 1000 ppm. The advantage is that bromine can be condensed directly from the steam. Air is used when seawater is the source of bromine because very large volumes of stripping gas are needed and steam would be too expensive. When air is used the bromine needs to be trapped in an alkaline or reducing solution to concentrate it.

Typical brines received at an Arkansas bromine plant have 3–5 g/L bromide, 200–250 g/L chloride, 0.15–0.20 g/L ammonia, 0.1–0.3 g/L hydrogen sulfide, 0.01–0.02 g/L iodide, and additionally may contain some dissolved organics, including natural gas and crude oil. The bromide-containing brine is first treated to remove natural gas, crude oil, and hydrogen sulfide prior to introduction into the contact tower (48).

The approximate composition of surface water in the Dead Sea in 1966 (49) was given as: 35 g/L calcium chloride; 130 g/L magnesium chloride; nearly 80 g/L sodium chloride; more than 10 g/L potassium chloride; nearly 4 g/L bromide; and about 1 g/L sulfate. At 400 m depth the bromide concentration was 6 g/L. Bromine in Israel is produced from the liquors left from potash production and the bromide content of these liquors is 14 g/L.

In the steaming-out process excess chlorine is used and recycled. The major process conditions that are measured and controlled are temperature, pressure, pH, and oxidation potential.

Materials that come in contact with wet halogens must be corrosion-resistant. Glass, ceramics, tantalum, and fluoropolymers are suitable materials. Granite has been used in steaming-out towers.

In the blowing-out process, used when the source of bromine is seawater, air is used instead of steam to strip bromine from solution. At the pH of seawater the liberated bromine hydrolyzes to hypobromous acid and bromide. Bromide traps bromine as the tribromide ion and little bromine is released. Before stripping, enough sulfuric acid is added to the seawater to reduce the pH to 3–3.5.

The exiting air containing bromine is absorbed in a sodium carbonate solution.

$$3\,Na_2CO_3 + 3\,Br_2 \rightarrow 5\,NaBr + NaBrO_3 + 3\,CO_2\uparrow$$

When the alkalinity of the absorbing solution becomes low it is moved to storage. Acidifying the absorbing solution with sulfuric acid reconstitutes the bromine which can then be steamed out.

$$NaBrO_3 + 5\,NaBr + 3\,H_2SO_4 \rightarrow 3\,Br_2 + 3\,Na_2SO_4 + 3\,H_2O$$

An alternative absorbing solution uses sulfur dioxide.

$$Br_2 + SO_2 + 2\,H_2O \rightarrow 2\,HBr + H_2SO_4$$

The bromine is recovered by oxidizing the bromide with chlorine and steaming it out of solution.

Treatment with sulfuric acid and fractional distillation are the main methods used to purify bromine. It is especially important to reduce the water content to less than 30 ppm to prevent corrosion of metal transportation and storage containers.

Newer Process Modifications. Patents describe a single-stage vacuum process (50) and a double-stage vacuum process (48) for recovering bromine from brines. The former is essentially the steaming-out process carried out at subatmospheric pressure. In the double-stage process the tail brines from the first stripping are stripped again under greater vacuum.

According to the patents, Arkansas brines reach the bromine plant at elevated temperatures and in the usual steaming-out process are further heated by steam to the boiling point. Additional steam is required to strip the bromine from the brine. Vacuum is used in the modified process, which, by matching the vapor pressure of the brine eliminates the need for steam to heat the brine. Because of the lower volume of steam used in the vacuum process, the capacity of a given size of contact tower is increased. A further benefit is that at the lower operating temperature of the vacuum process, chlorine undergoes fewer side reactions and less hydrolysis so chlorine use can be reduced. In the two-stage process (Fig. 2), a second steam stripping of the tail brine is done. Other claimed advantages of the vacuum process are a reduction in the amount of lime required to treat the spent brine, lower plant maintenance costs, and decreased waste gases.

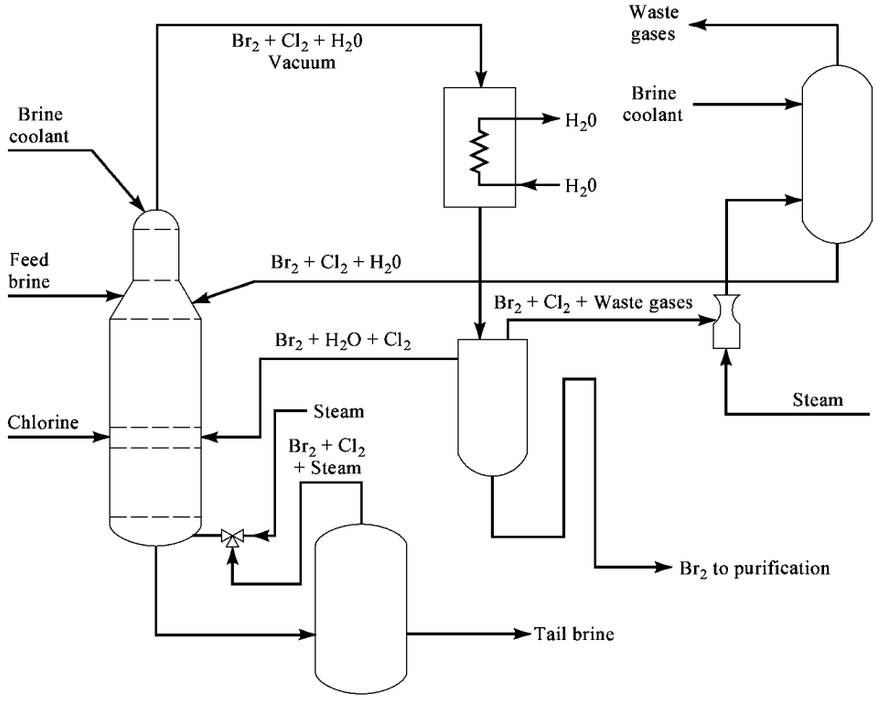


Fig. 2. Schematic of a two-stage vacuum bromine steaming-out process.

Economic Aspects

Facilities for manufacturing bromine are primarily located near sources of natural brines or bitterns containing usable levels of bromine. In 1990, the United States had seven bromine plants owned by four companies. Six of the plants are in southern Arkansas and are operated by two U.S. producers: Great Lakes Chemical Corporation and Ethyl Corporation.

The costs of building and maintaining a bromine plant are high because of the corrosiveness of brine solutions which contain chlorine and bromine and require special materials of construction. The principal operating expenses are for pumping, steam, environmental costs, energy, and chlorine. The plants are very capital intensive.

Figure 3 shows the prices of bromine in tank car quantities from 1976 to 1990. Although the price rose 99% over these years, an average of 5.0% a year, when inflation is taken into account, the price in constant dollars actually fell slightly over that period (51). Estimates of bromine production around the world are shown in Table 3.

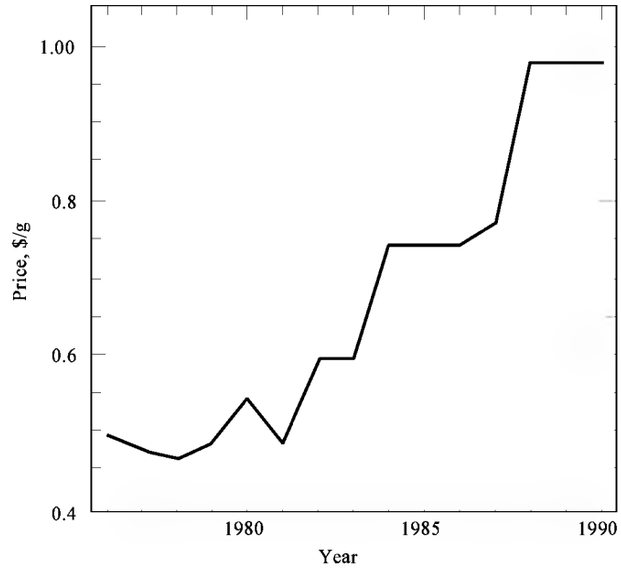


Fig. 3. Average U.S. bromine prices.

Table 3. Annual Bromine Production in Thousands of Metric Tons[a]

Country	1976	1978	1980	1982	1984	1986	1988	1990
United States	234.0	223.3	189.1	200.1	192.5	140.6	163.3	177.0
France	16.7	17.9	18.2	10.0	12.5	19.0	18.0	18.0
Germany	4.6	4.3	4.4	3.4	3.5	2.5	2.5	3.0
India	0.5	0.5	0.4	0.4	0.4	1.2	1.2	1.3
Israel	23.1	38.1	48.6	77.0	99.2	105.0	118.0	135.0
Italy	0.6	0.7	0.7	0.7	0.6	0.5	0.5	0.4
Japan	13.3	13.3	13.3	13.3	13.3	15.0	15.0	15.0
Spain	0.5	0.5	0.5	0.4	0.4	0.3	0.3	0.3
United Kingdom	33.0	27.7	29.1	32.8	28.7	26.0	27.1	28.0
Russia	70.0	72.0	74.0	75.0	77.0	65.0	65.0	60.0
World Total[b]	*396.1*	*398.0*	*378.1*	*413.5*	*427.9*	*375.1*	*410.9*	*438.0*

[a] Refs. 51, 52.

[b] Data may not add to totals shown because of independent rounding.

Figure 4 shows U.S. bromine production with respect to bromine production in the rest of the world. Israel, especially, has increased its production in recent years (51,52). Between 1976 and 1990 U.S. production fell from 234,000 to 177,000 metric tons; Israel's production increased from 23,000 to 135,000 metric tons over that period.

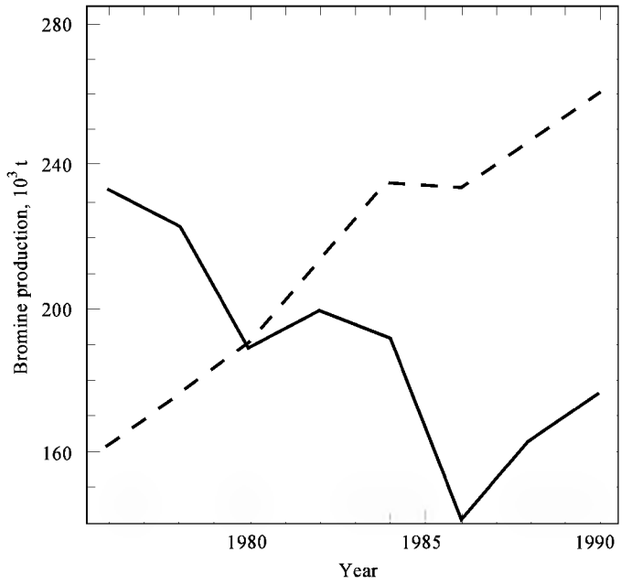


Fig. 4. Annual U.S. (—) and world ( ) bromine production.

Figure 5 shows import and export trends (52,53).

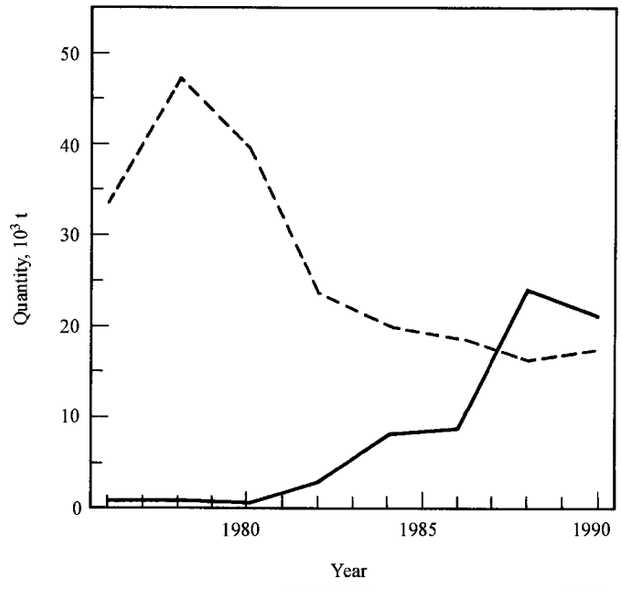


Fig. 5. Annual U.S. imports (—) and exports (- - -) of bromine and bromine compounds.

Requirements and Specifications

Typical specifications for bromine produced in a modern plant (54) generally exceed the ACS requirements for bromine used as a reagent chemical (55) (Table 4).

Table 4. Bromine Specification

Parameter	ACS requirements	Product specifications
bromine content, wt %[a]	99.5	99.9
specific gravity, 20 15°C[a]		3.1
water, ppm[b]		30
chlorine, ppm[b]	500	100
organic halogen compounds, ppm[a]	[c]	80
nonvolatile matter, ppm[a]	50	30
iodine	10	[c]
sulfur (as S)	10	[c]
heavy metals (as Pb)	2	[c]
nickel	5	[c]

[a] Minimum value.

[b] Maximum value.

[c] Must pass ACS test.

Analytical Methods

To assay liquid bromine, an ampule of bromine is crushed under the surface of an aqueous potassium iodide solution and the resultant iodine titrated with standard sodium thiosulfate.

$$2\,I^- + Br_2 \rightarrow I_2 + 2\,Br^-$$

$$I_2 + 2\,Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2\,NaI$$

Bromine vapor can be analyzed by the same procedure. The specific gravity of bromine is determined by hydrometer (54).

Bromine and bromides can be detected qualitatively by a number of methods. In higher concentrations bromine forms colored solutions in solvents such as carbon tetrachloride *[56-23-5]* and carbon disulfide *[75-15-0]*. Bromine reacts with yellow disodium fluorescein *[518-47-8]* to form red disodium tetrabromofluorescein (eosin) *[548-26-5]*, $C_{20}H_{8}Br_4Na_2O_5$. As little as 0.3 μg of bromide can be detected and chlorides do not interfere (56). Bromine reacts with platinum sulfate *[7446-29-9]*, $Pt(SO_4)_2$, solution to form red to brown crystals of potassium hexabromoplatinate *[16920-93-7]*, K_2PtBr_6 (57).

Impurities in bromine may be determined quantitatively (54). Weighing the residue after evaporation of a bromine sample yields the total nonvolatile matter. After removing the bromine, chloride ion may be determined by titration with mercuric nitrate, and iodide ion by titration with thiosulfate; water and organic compounds may be detected by infrared spectroscopy; sulfur may be determined turbidimetrically as barium sulfate; and heavy metals may be determined colorimetrically after conversion to sulfides.

Quantitative methods for determining bromide include: the Mohr method, using $AgNO_3$ titrant and potassium chromate indicator; the Volhard method using excess $AgNO_3$ titrated with potassium thiocyanate and ferric ammonium sulfate indicator; Fajans method with $AgNO_3$, as titrant, eosin as absorption indicator; silver nitrate titrant with the end point determined potentiometrically using a silver indicator electrode; and a gravimetric method as AgBr. Bromides can be detected in acidic solutions by titrating with mercuric nitrate using sodium nitroprusside indicator. Trace amounts of bromides can be determined quantitatively by the van der Meulen method, which is useful in presence of large amounts of chloride, the bromide is oxidized to bromate and determined iodometrically; by constant-current and constant-potential coulometry, used for fractions of a milligram up to several grams of bromide; by ion chromography, which is useful for detecting bromide in the presence of other ions; by polography, useful for microgram quantities (58); by spectrophotometric methods useful for microgram quantities in the presence of chloride (58); and by activation analysis with thermal neutrons which is useful for nanogram quantities.

Bromine in organic compounds can be determined chemically following oxidation of the organic compounds and reduction of the bromine to bromide. In the Shoniger method a few milligrams of sample is burned inside of a stoppered Erlenmeyer flask filled with oxygen. After ignition by electrical or other means, the combustion products are absorbed and the bromine content is determined acidimetrically (59,60). An alternative method employs a fusion with sodium peroxide in a Paar bomb. Infrared spectroscopy allows the determination of bromine with an accuracy of about 1%. Neutron activation, x-ray fluorescence, ir spectroscopy, and atomic emission spectroscopy are also used to determine bromine in organic materials.

Bromine is used as an analytical reagent to determine the amount of unsaturation in organic compounds because carbon–carbon double bonds add bromine quantitatively, and for phenols which add bromine in the ortho and para positions. Standard bromine is added in excess and the amount unreacted is determined by an indirect iodine titration. Bromine is also used to oxidize several elements, such as Tl(I) to Tl(III). Excess bromine is removed by adding phenol. Bromine plus an acid, such as nitric and/or hydrochloric, provides an oxidizing acid mixture useful in dissolving metal or mineral samples prior to analysis for sulfur.

Health, Safety, and Handling

Consequences of Exposure. Bromine has a sharp, penetrating odor. The OSHA/ACGIH threshold limit value–time-weighted average for an 8-h workday and 40-h workweek is 0.1 ppm in air (61). Monitors are available for determining bromine concentrations in air. Concentrations of about 1 ppm are unpleasant and cause eyes to water; 10 ppm are intolerable. Inhalation of 10 ppm and higher concentrations of bromine causes severe burns to the respiratory tract and is highly toxic. Symptoms of overexposure include coughing, nose bleed, feeling of oppression, dizziness, headache, and possibly delayed abdominal pain and diarrhea. Pneumonia may be a late complication of severe exposure.

Liquid bromine produces a mild cooling sensation on first contact with the skin. This is followed by a sensation of heat. If bromine is not removed immediately by flooding with water, the skin becomes red and finally brown, resulting in a deep burn that heals slowly. Contact with concentrated vapor can also cause burns and blisters. For very small areas of contact in the laboratory, a 10% solution of sodium thiosulfate in water can neutralize bromine and such a solution should be available when working with bromine. Bromine is especially hazardous to the tissues of the eyes where severely painful and destructive burns may result from contact with either liquid or concentrated vapor. Ingestion causes severe burns to the gastrointestinal tract (62,63).

Detection of Bromine Vapor. Bromine vapor in air can be monitored by using an oxidant monitor instrument that sounds an alarm when a certain level is reached. An oxidant monitor operates on an amperometric principle. The bromine oxidizes potassium iodide in solution, producing an electrical output by depolarizing one sensor electrode. Detector tubes, useful for determining the level of respiratory protection required, contain *o*-toluidine that produces a yellow-orange stain when reacted with bromine. These tubes and sample pumps are available through safety supply companies (54). The useful concentration range is 0.2–30 ppm.

Protective Equipment. For handling bromine in the laboratory the minimum safety equipment should include chemical goggles, rubber gloves (Buna-*N* or neoprene rubber), laboratory coat, and fume hood. For handling bromine in a plant, safety equipment should include hard hat, goggles, neoprene full coverage slicker, Buna-*N* or neoprene rubber gloves, and neoprene boots. For escaping from an area where a bromine release has occurred, a full face respirator with an organic vapor–acid gas canister is desirable. For emergency work in an area with bromine concentrations above 0.1 ppm, a self-contained breathing apparatus can be used until the air supply gets low. For longer term work in elevated bromine concentrations, an air-line respirator is essential.

Reactivity. Bromine is nonflammable but may ignite combustibles, such as dry grass, on contact. Handling bromine in a wet atmosphere, extreme heat, and temperatures low enough to cause bromine to solidify (−6°C) should be avoided. Bromine should be stored in a cool, dry area away from heat. Materials that should not be permitted to contact bromine include combustibles, liquid ammonia, aluminum, titanium, mercury, sodium, potassium, and magnesium. Bromine attacks some forms of plastics, rubber, and coatings (62).

Spills and Disposal Procedures. If a spill occurs outdoors, personnel should stay upwind of it. If the spill is in a diked area it may be possible to recover much of the bromine, otherwise it should be absorbed with appropriate material. A water spray can be used to control bromine vapors and a mild ammonia atmosphere helps to neutralize bromine vapors. Small spills may be neutralized with lime water slurry or soda ash and flushed with large amounts of cold water.

Under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)/RCRA regulations in effect at the end of 1986 bromine is regulated as a hazardous waste or material. Therefore, it must be disposed of in an approved hazardous waste facility in compliance with EPA and/or other applicable local, state, and federal regulations and should be handled in a manner acceptable to good waste management practice. The reportable quantity is 45.4 kg for corrosivity (62).

Materials of Construction. Glass has excellent corrosion-resistance to wet or dry bromine. Lead is very useful for bromine service if water is less than 70 ppm. The bromine corrosion rate increases with concentrations of water and organics. Tantalum and niobium have excellent corrosion-resistance to wet or dry bromine. Nickel has useful resistance for dry bromine but is rapidly attacked by wet bromine. The fluoropolymers Kynar, Halar, and Teflon are highly resistant to bromine but are somewhat permeable. The rate depends on temperature, pressure, and structure (density) of fluoropolymer (63).

Storage and Transportation. Bromine in bulk quantities is shipped domestically in 7570 L and 15,140 L lead-lined pressure tank cars or

6435–6813 L nickel-clad pressure tank trailers. The trailers must be filled at least 92% full to prevent inertia effects of the heavy liquid while on the highway. International shipments are in 6245 L lead-lined International Standards Organization (ISO) tanks. The relatively high freezing point of bromine (7.25°C) may cause some problems in shipping and storage. If bromine has frozen in a tank car, it is necessary to circulate warm (below 54°C) water through the heating coils.

Dry nitrogen gas is recommended for use in pressure transferring bromine, although dry (40°C dew point) air may be used. The gas used to pad the bromine in the storage tank must be absolutely dry or severe corrosion results. Dry bromine picks up water from air having a dew point of 70°C. When exposed to a high humidity atmosphere the water content of bromine can exceed 300 ppm. Bromine is nonreactive to lead, monel, and a few other alloys when water content is below 30 ppm. If the water content increases above 70 ppm, corrosivity to many metals increases greatly. Fluorinated plastics are widely used in equipment, piping, valves, and gaskets.

Uses

An important use of bromine compounds is in the production of flame retardants (qv). These are of the additive-type, which is physically blended into polymers, and the reactive-type, which chemically reacts during the formation of the polymer. Bromine compounds are also used in fire extinguishers. Brominated polymers are used in flame retardant applications and bromine-containing epoxy sealants are used in semiconductor devices (see SEMICONDUCTORS).

Bromine has some use in swimming pools and in bleaching. It is also a disinfectant for cooling water and wastewater. Its main use is as a chemical reactant. Bromine compounds are frequently intermediates in the production of other organic chemicals. Bromine is found in certain dyes. Bromides have been used for many years in the pharmaceutical industry as sedatives and as intermediates for drugs. Some therapeutic powers are claimed for certain iodine–bromine spa waters. Alkali bromides are used in the photographic industry. Bromine is used in making some perfumes and certain bromine compounds are disinfectants, eg, bromochlorodimethylhydantoin, which is used in swimming pools and spas.

Zinc–bromine storage batteries (qv) are under development as load-leveling devices in electric utilities (64). Photovoltaic batteries have been made of selenium or boron doped with bromine. Graphite fibers and certain polymers can be made electrically conductive by being doped with bromine. Bromine is used in quartz–halide light bulbs. Bromine is used to etch aluminum, copper, and semi-conductors. Bromine and its salts are known to recover gold and other precious metals from their ores. Bromine can be used to desulfurize fine coal (see COAL CONVERSION PROCESSES). Table 5 shows estimates of the primary uses of bromine.

Table 5. U.S. Bromine Demand According to Use[a]

	Bromine, 10^3 t (%)				
Use	1978	1981	1984	1987	1990
ethylene dibromide synthesis	124 (55)	76 (40)	39 (20)	34 (20)	27 (15)
flame retardants	56 (25)	47 (25)	58 (30)	45 (27)	48 (27)
inorganic bromides	23 (10)	38 (20)	54 (28)	17 (10)	9 (5)
agricultural chemicals		9 (5)	19 (10)	25 (15)	27 (15)
completion drilling fluids					18 (10)
exports			8 (4)	8 (5)	12 (7)
water treatment chemicals				15 (9)	9 (5)
other	23 (10)	19 (10)	15 (8)	23 (14)	29 (16)
Total	*226 (100)*	*189 (100)*	*193 (100)*	*167 (100)*	*179 (100)*

[a] Ref. 65.

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BROMINE COMPOUNDS

Inorganic Compounds

Bromamines. Bromamide *[14519-10-9]*, NH_2Br, is formed from bromine and liquid ammonia:

$$Br_2 + 2\,NH_3 \rightarrow NH_2Br + NH_4^+ + Br^-$$

By evaporating a mixture of bromine and ammonia at low temperatures, nitrogen bromide *[15162-90-0]*, NBr_3, is obtained as the ammoniate $NBr_3 \cdot 6NH_3$. This compound decomposes explosively when warmed to room temperature. NH_2Br and bromimide *[14519-03-0]*, $NHBr_2$, are formed when bromine reacts with ammonia in ether solution at low temperatures. These products have not been isolated (1).

In swimming pools disinfected by bromine, bromamide and bromimide can form. These compounds have about half the disinfecting power of HOBr giving bromine an advantage compared to chlorine. Chloramide and chlorimide have 80 to 100 times less disinfecting power than HOCl.

Bromides.

Hydrogen Bromide. Hydrogen bromide *[10035-10-6]*, HBr, (hydrobromic acid), is a colorless gas that fumes strongly in moist air; mp, −86°C (2); liquid density, 2.152 g/mL; bp, −67°C; heat capacity for the solid at −91°C, 636 J/(kg·K) (152 cal/(kg·K)), liquid, 737 J/(kg·K) (176 cal/(kg·K)), gas at 27°C, 356 J/(kg·K) (85 cal/(kg·K)); heat of fusion at mp, 29.8 kJ/kg (7.12 kcal/kg); heat of vaporization at −66.7°C, 218 kJ/kg (52 kcal/kg); critical temperature, 89.8°C; critical pressure, 8510 kPa (84 atm). The gas is highly soluble in water, forming azeotropic mixtures the compositions of which have been determined at various pressures (3). At normal atmospheric pressure the boiling point is 124.3°C and the HBr content is 47.63%. This mixture has a melting point of −11°C and a density of 1.482 g/mL at 25°C. At very low temperatures hydrogen bromide forms crystalline hydrates with 1, 2, 3, and 4 moles of water (4).

The manufacture of HBr gas involves burning a mixture of hydrogen and bromine vapor. Alternatively, platinized asbestos or silica gel can catalyze this reaction. The vapor is passed through hot, activated charcoal or iron to remove free bromine (5), and is either liquefied by cooling for shipment in cylinders, or is absorbed in water. In the laboratory several methods are available for preparing HBr solutions: reaction of bromine with sulfur dioxide and water followed by distillation; distillation of HBr from potassium bromide and dilute sulfuric acid; or passing an alkali bromide solution through the hydrogen form of a cation-exchange resin that is suitable for dilute solutions.

Hydrobromic acid is one of the strongest mineral acids. It is a more effective solvent for some ore minerals than hydrochloric acid because of its higher boiling point and stronger reducing action. Certain higher oxides such as ceric oxide are readily dissolved. With the bromides of several metals, the acid forms complexes such as hydrogen tetrabromoferrate *[19567-68-1]*, $HFeBr_4$, amber; hydrogen tribromocuprate *[31415-59-5]*, $HCuBr_3$, violet, etc. Bromine is very soluble in strong aqueous hydrobromic acid.

The liquid and vapors of hydrobromic acid are highly corrosive to tissue. The threshold limit value for HBr gas in an 8-h day is 3 ppm time-weighted average. Inhalation of vapor is so irritating to the nose and throat that a person does not voluntarily remain in an area when vapors are present in hazardous concentrations. Symptoms of overexposure to HBr include coughing, choking, burning in the throat, wheezing, or asphyxia. Ingestion causes severe burns of the mouth and stomach and skin contact can cause severe burns. In the case of liquid or vapor contact with eyes, permanent damage may result. Suitable safety equipment should be used when handling HBr and a safety shower and eye bath should be available.

HBr reacts with metals, producing highly explosive hydrogen gas. If a leak or spill occurs, exposure to the vapors should be avoided. If a high concentration of aqueous acid is accidentally spilled, it should be diluted immediately with water to reduce fuming prior to neutralization. Hydrobromic acid may be neutralized with soda ash or lime sprinkled over the contaminated area. An aqueous solution of sodium hydroxide may also be used to neutralize the diluted acid.

Most metals, concrete, and other construction materials are corroded by hydrobromic acid. Suitable materials of construction include some fiber glass-reinforced plastics, some chemically resistant rubbers, PVC, Teflon, polypropylene, and ceramic-, rubber-, and glass-lined steel. Metals that are used include Hastelloy B, Hastelloy C, tantalum, and titanium. The Hastelloys can only be used at ambient temperatures. Liquid hydrogen bromide under pressure in glass at or above room temperature can attack the glass resulting in unexpected shattering.

Technical 48% and 62% acids are colorless to light yellow liquids available in drums, 15,140-L tank trailers, and 37,850-L tank cars. They are classified under DOT regulations as corrosive materials. Anhydrous hydrogen bromide is available in cylinders, under its vapor pressure of approximately 2.4 MPa (350 psi) at 25°C. It is classified as a nonflammable gas.

A considerable amount of hydrobromic acid is consumed in the manufacture of inorganic bromides, as well as in the synthesis of alkyl bromides from alcohols. The acid can also be used to hydrobrominate olefins (qv). The addition can take place by an ionic mechanism, usually in a polar solvent, according to Markownikoff's rule to yield a secondary alkyl bromide. Under the influence of a free-radical catalyst, in aprotic, nonpolar solvents, dry hydrogen bromide reacts with an α-olefin to produce a primary alkyl bromide as the predominant product. Primary alkyl bromides are useful in synthesizing other compounds and are 40–60 times as reactive as the corresponding chlorides (6).

Hydrogen bromide adds to acetylene to form vinyl bromide or ethylidene bromide, depending on stoichiometry. The acid cleaves acyclic and cyclic ethers. It adds to the cyclopropane group by ring-opening. Additions to quinones afford bromohydroquinones. Hydrobromic acid and aldehydes can be used to introduce bromoalkyl groups into various molecules. For example, reaction with formaldehyde and an alcohol produces a bromomethyl ether. Bromomethylation of aromatic nuclei can be carried out with formaldehyde and hydrobromic acid (6).

In the petroleum (qv) industry hydrogen bromide can serve as an alkylation catalyst. It is claimed as a catalyst in the controlled oxidation of aliphatic and alicyclic hydrocarbons to ketones, acids, and peroxides (7,8). Applications of HBr with NH_4Br (9) or with H_2S and HCl (10) as promoters for the dehydrogenation of butene to butadiene have been described, and either HBr or HCl can be used in the vapor-phase ortho methylation of phenol with methanol over alumina (11). Various patents dealing with catalytic activity of HCl also cover the use of HBr. An important reaction of HBr in organic syntheses is the replacement of aliphatic chlorine by bromine in the presence of an aluminum catalyst (12). Small quantities of hydrobromic acid are employed in analytical chemistry.

Other Bromides. Alkali and alkaline earth bromides can be prepared by neutralizing a solution of the corresponding hydroxide or carbonate with hydrobromic acid. Alternatively, bromine and a reducing agent such as ammonia are used in the van der Meulen process (13):

$$3\,K_2CO_3 + 3\,Br_2 + 2\,NH_3 \rightarrow 6\,KBr + N_2 + 3\,CO_2 + 3\,H_2O$$

Ammonium bromide *[12124-97-9]* can be prepared by the direct reaction of bromine with aqueous ammonia:

$$3\,Br_2 + 8\,NH_4OH \rightarrow 6\,NH_4Br + N_2 + 8\,H_2O$$

Anhydrous lithium bromide *[7550-35-8]*, LiBr, is a desiccant useful in the industrial drying of air. When it contains sufficient moisture it can be a

humectant. Sodium bromide *[7647-15-6]*, NaBr, if used in conjunction with an oxidizer, such as chlorine or sodium hypochlorite, is an effective biocide in cooling water systems. A water solution of sodium bromide can also function as an oil well completion fluid or, with an oxidizer, as a bleaching agent and it is an intermediate for the manufacture of various chemicals. Sodium bromide and potassium bromide *[7758-02-3]*, KBr, are used to prepare light-sensitive emulsions for photography. Potassium bromide is also used in process engraving. It finds use in infrared spectroscopy in adsorption cell windows and as a solid sample matrix. These three bromides have medical applications as sedatives, hypnotics, or anticonvulsants. Rubidium bromide *[7789-39-1]*, RbBr, is claimed as a component of x-ray intensifier screens (14). Cesium bromide *[7787-69-1]*, CsBr, finds application in x-ray fluorescent screens, spectrometer prisms, and adsorption-cell windows.

Beryllium bromide *[7787-46-4]*, $BeBr_2$, is claimed as an adhesive for poly(vinyl alcohol) (15). Magnesium bromide *[7789-48-2]*, $MgBr_2$, is used in organic synthesis. A concentrated solution of calcium bromide *[7789-41-5]*, $CaBr_2$, in water has a specific gravity of at least 1.7 and is useful as a completion, workover, and packer fluid in oil well drilling and maintenance. Other applications include water treatment, bleaching, photography, gravity separation fluid, electrical conductivity fluid, and an intermediate for the manufacture of various chemicals. In medicine magnesium bromide and calcium bromide are sedatives and anticonvulsants. Strontium bromide *[10476-81-0]*, $SrBr_2$, has been used as an anticonvulsant. Barium bromide *[10553-31-8]*, $BaBr_2$, is a reactant for the manufacture of other bromides and in the preparation of phosphors.

Cerous bromide *[14457-87-5]*, $CeBr_3$, and praseodymium bromide *[13536-53-3]*, $PrBr_3$, are claimed to be suitable for a molten salt bath used for the reduction of uranium oxide by magnesium (16). $PrBr_3$ is claimed to be a light filter in a cathode ray tube (17).

Titanium bromide *[7789-68-6]*, $TiBr_4$, is claimed as a catalyst for olefin polymerizations (18). Chromous bromide *[10049-25-9]*, $CrBr_2$, is used in chromizing. Chromic bromide *[10031-25-1]*, $CrBr_3$, and tungsten bromide *[13701-86-5]*, WBr , are catalysts for polymerizing olefins (19). Manganese bromide *[13446-03-2]*, $MnBr_2$, is a catalyst for the formation of aromatic aldehydes from alkylbenzenes (20) and phthalic acids from xylenes (21). It is also claimed as a catalyst in the ammoxidation conversion of *o*-xylene to phthalimide (22).

Ferrous bromide *[7789-46-0]*, $FeBr_2$, is a polymerization catalyst. Ferric bromide *[10031-26-2]*, $FeBr_3$ is a catalyst for organic reactions, particularly in brominations of aromatic compounds. Cobaltous bromide *[7789-43-7]*, $CoBr_2$, is used in hydrometers and as a catalyst for organic reactions. Rhodium bromide *[15608-29-4]*, $RhBr_3$, is claimed as a catalyst for carbonylating methanol (qv) to acetic acid (see ACETIC ACID AND DERIVATIVES) (23). Nickel bromide *[13462-88-9]*, $NiBr_2$, is a catalyst in dimerizing butadiene (24), in condensing butadiene onto ring systems and benzyl ketones (25,26), for oxidizing secondary alcohols to ketones (qv) (27), and for preparing biaryls from aryl iodides (28). Palladium bromide *[13444-94-5]*, $PdBr_2$, is a catalyst for various carbonylation reactions (29–31). Platinum bromide *[13455-12-4]*, $PtBr_2$, is a general dehydrodimerization catalyst for boron hydrides and carboranes (32,33) (see BORON COMPOUNDS).

Cuprous bromide *[7787-70-4]*, CuBr, is a catalyst for organic reactions. Cupric bromide *[7789-45-9]*, $CuBr_2$, is used as an intensifier in photography, as a brominating agent in organic synthesis, as a humidity indicator, as a wood preservative, as a stabilizer for acetylated polyformaldehyde, and in solid-electrolyte batteries. Silver bromide *[7785-23-1]*, AgBr, is used in photography, as a topical antiinfective, and as an astringent. Gold tribromide *[10294-28-7]*, $AuBr_3$, is claimed as a component of a sensor for halogenated gases (34). Bromoauric acid *[17083-68-0]*, $HAuBr_4$, is a catalyst in the selective oxidation of sulfides to sulfoxides by nitric acid (35). Sodium tetrabromoaurate *[52495-41-7]*, $Na[AuBr_4]$ and potassium tetrabromoaurate *[13966-47-7]*, $K[AuBr_4]$, are claimed to be useful in gold-coating solutions (36).

Zinc bromide *[7699-45-8]*, $ZnBr_2$, is consumed to make silver bromide collodion emulsions for photography, in radiation shielding, in gravity separation, as an electrical conductivity fluid, and as an intermediate for the manufacture of various chemicals. Storage batteries with a zinc bromide electrolyte are under development for use as load-leveling devices in electric utilities and as electric car batteries (37). Because of their high density, zinc bromide, along with other bromides such as NaBr or $CaBr_2$, solutions are produced commercially to be used as completion, workover, and packer fluids in oil well drilling and maintenance. Mercurous bromide *[10031-18-2]*, Hg_2Br_2, reacts with HBr to form hydrogen (qv) quantitatively (38).

Boron tribromide *[10294-33-4]*, BBr_3, is used in the manufacture of diborane and in the production of ultra high purity boron (see BORON, ELEMENTAL; BORON COMPOUNDS). Anhydrous aluminum bromide *[7727-15-3]*, $AlBr_3$, is used as an acid catalyst in organic syntheses where it is more reactive and more soluble in organic solvents than $AlCl_3$. Thallium bromide *[7789-40-4]*, TlBr, is claimed as a component in radiographic image conversion panels (39).

Silicon tetrabromide *[7789-66-4]*, $SiBr_4$, and tribromosilane *[7789-57-3]*, $SiHBr_3$, are used in a process to make high purity silicon (40). Stannous bromide *[10031-24-0]*, $SnBr_2$, is claimed as a catalyst in preparing a lubricant antioxidant (41). Stannic bromide *[7789-67-5]*, $SnBr_4$, is used in the metallurgical separation of minerals (42).

Ammonium bromide *[12124-97-9]*, NH_4Br, is used in photography, process engraving and lithography, fireproofing of wood, corrosion inhibitors, and in medicine as a sedative. Phosphorus tribromide *[7789-60-8]*, PBr_3, converts primary alcohols into bromides (43). Phosphorus pentabromide *[7789-69-7]*, PBr_5, is a brominating agent for converting organic acids to acyl bromides. It also can be used to convert phenols (44) and secondary alcohols into bromides (45). Bismuth bromide *[7787-58-8]*, $BiBr_3$, is claimed as a catalyst for dehydrating cyclohexanol to cyclohexene (46). It is also claimed as part of a solid electrolyte in primary lithium batteries (47). Selenium tetrabromide *[7789-65-3]*, $SeBr_4$, is claimed as a dopant for a photoreceptor for electrophotography (qv) (48) and also as an additive for a rapid bright silver electroplating (qv) bath (49). Tellurium tetrabromide *[10031-27-3]*, $TeBr_4$, is a catalyst for the synthesis of organic acids (50,51).

Thionyl bromide *[507-16-4]*, $SOBr_2$, is used to convert alcohols to bromides (52).

Bromine Halides. Bromine and chlorine react reversibly in the liquid or vapor states to form bromine chloride *[13863-41-7]*, BrCl. In an equimolar mixture of bromine and chlorine vapors at room temperature, about 60 mol % of the halogen is present as BrCl (53). This proportion does not change much with temperature. Bromine chloride is a dark red, fuming, lachrimatory liquid with a boiling point of 5°C. A similar but somewhat more stable compound, iodine bromide *[7789-33-5]*, IBr, is formed from bromine and iodine. There is also evidence for the existence of a tribromo complex, IBr_3, iodine tribromide *[7789-58-4]*. These compounds are soluble in carbon tetrachloride or acetic acid and are used as halogenating agents for organic substances (54,55).

Bromine chloride adds to olefins giving bromochloro compounds. BrCl can also displace hydrogen yielding an organic bromide and hydrogen chloride. The use of bromine chloride rather than chlorine as a disinfectant in wastewater treatment has the advantages of maintaining activity over a wider pH range, more rapid disinfection, effectiveness at lower residual concentrations, and lower aquatic toxicity (56). The time-weighted average concentration of bromine chloride should not exceed 0.1 ppm for an 8-h day. Suitable materials of construction for shipping and storage of BrCl are low carbon steel or nickel, or its alloys, such as Monel (56). Bromine chloride is used as a brominating agent in the preparation of fire-retardant chemicals, pharmaceuticals, high density brominated liquids, agricultural chemicals, dyes, bleaching agents, and in water treatment, eg, in cooling towers and effluent streams from sewage plants.

Bromine monofluoride *[13863-59-7]*, BrF, can be prepared by the direct reaction of Br_2 and F_2, but because it readily disproportionates it has never been prepared in pure form (57). However, BrF can be prepared *in situ* by the reaction of Br_2 with AgF in benzene (58) or by the reaction of *N*-bromoacetamide and HF in ether (59). BrF adds to simple alkenes at room temperature to give products of trans-addition. Bromine trifluoride *[7787-71-5]*, BrF_3, can be formed from gaseous fluorine and liquid bromine (60). Bromine pentafluoride *[7789-30-2]*, BrF_5, is formed from the reaction of BrF_3 vapor with gaseous fluorine at 200°C (60). The tri- and pentafluorides are commercially available. As strong fluorinating agents they are useful in

organic syntheses (61–63) and in forming uranium fluorides, both for isotope enrichment (64,65) and for fuel element reprocessing (66). With alkali fluorides they form salts $MBrF_4$ and MBrF analogous, in regard to the bromine valence state, to bromites and bromates.

The time-weighted, 8-h average limit for exposure to bromine pentafluoride is 0.1 ppm (67). Materials of construction suitable for use with the bromine fluorides include nickel, Monel metal, or Teflon. For shipping, bromine trifluoride and pentafluoride are classified as oxidizers under DOT regulations. The trifluoride also requires a poison label.

Bromine Oxides, Acids, and Salts.

Oxides. None of the oxides of bromine is stable at ordinary temperatures and none has any practical use. When Br_2 in CF_3Cl is oxidized with ozone at 78°C, bromine dioxide *[21308-80-5]*, BrO_2, is formed. This yellow solid is thermally unstable above 40°C and decomposes violently at ~0°C. Dibromine oxide *[21308-80-5]*, Br_2O, can be obtained by low temperature decomposition of BrO_2 in vacuum, or by reaction of Br_2 with Hg_2O. It is a brown solid below 17.5°C but appears to be unstable above 60°C. Br_2O, like Cl_2O, is a bent molecule. Various other bromine oxides, eg, Br_2O_3, Br_2O_5, Br_3O_8, and BrO_3 have been reported but none has been fully characterized and all are unstable (68).

Acids and Salts. The oxygen acids of bromine are strong oxidants but at ordinary temperatures are stable only in solution. An aqueous solution of hypobromous acid *[13517-11-8]* may be prepared by treating bromine water with silver oxide or mercuric oxide (69):

$$2\,Br_2 + Ag_2O + H_2O \rightarrow 2\,HOBr + 2\,AgBr$$

$$2\,Br_2 + HgO + H_2O \rightarrow 2\,HOBr + HgBr_2$$

A more concentrated solution of HOBr can be prepared by filtration of one of the above solutions and distillation in vacuum. Or the mercuric oxide reaction can be carried out in Freon 11 without water, yielding a solution of bromine monoxide which is filtered and hydrolyzed. Hypobromous acid is slightly ionized; its dissociation constant at 25°C is 2×10^{9}.

Hypobromites, the salts of hypobromous acid, do not keep well because they gradually disproportionate to bromide and bromate. Solutions are best prepared as needed from bromine and alkali with cooling. Because disproportionation is catalyzed by cobalt, nickel, and copper (70), these impurities should be avoided. Solid alkaline earth hypobromites, or more properly, bromide hypobromites such as calcium bromide hypobromite *[67530-61-4]*, CaBr(OBr), have been known for many years, but the pure crystalline hydrates sodium hypobromite pentahydrate *[13824-96-9]*, $NaOBr \cdot 5H_2O$, and potassium hypobromite trihydrate *[13824-97-0]*, $KOBr \cdot 3H_2O$, were not described until 1952 (71). Hypobromites are strong bleaching agents, similar to hypochlorites.

The existence of bromous acid *[7486-26-2]*, HOBrO, is doubtful (72). The controlled disproportionation of cold concentrated alkaline hypobromite solutions can yield BrO ; ammonia or acetone is used to destroy residual BrO (73). Lithium bromite *[14518-92-4]*, $LiBrO_2$, sodium bromite *[7486-26-2]*, $NaBrO_2$, potassium bromite *[76908-17-3]*, $KBrO_2$, and barium bromite *[14899-01-5]*, $Ba(BrO_2)_2$, have been crystallized from such solutions. Sodium bromite is used as a desizing agent in the textile industry. Anhydrous $LiBrO_2$ and $Ba(BrO_2)_2$ have been prepared by heating (73).

$$2\,LiBrO_3 + LiBr \xrightarrow{190^\circ C} 3\,LiBrO_2$$

$$Ba(BrO_3)_2 \xrightarrow{250^\circ C} Ba(BrO_2)_2 + O_2$$

Methods for the analysis of hypobromite–bromite mixtures are given (74).

Bromic acid *[7789-31-3]*, $HBrO_3$, can be prepared in solution by the reaction of barium bromate with sulfuric acid. In an alternative procedure, an alkali bromate solution is passed through a cation-exchange resin in hydrogen form. The resulting acid can be concentrated in vacuum to about 50% $HBrO_3$. Stronger solutions are not stable and the 50% solution begins to decompose around 40°C. Bromic acid is a strong acid ($pK < 0$). It is also a strong oxidant, with a standard potential of 1.47 V for the reaction $HBrO_3 \rightarrow \frac{1}{2}Br_2$ in acid solution.

Bromates are stable in storage. They have various uses based on their oxidizing power. Bromates can be formed by the disproportionation of bromine in basic solution:

$$3\,Br_2 + 6\,OH \rightarrow BrO_3 + 5\,Br + 3\,H_2O$$

Boiling the solution speeds the conversion of intermediate hypobromites and bromites to bromate. The less soluble bromate can be separated from the halide by fractional crystallization. A method that is often more economical is the oxidation of bromides into bromates by hypochlorites in aqueous solution. This can be done by passing chlorine into an alkaline bromide solution (75):

$$3\,Cl_2 + 6\,OH + Br \rightarrow BrO_3 + 6\,Cl + 3\,H_2O$$

Another method for preparing alkali bromates is by electrolysis of bromine in alkali solutions. Anodes coated with PbO_2 are used and a small amount of dichromate is added to prevent reduction of BrO at the cathode (76).

Bromates represent a potential fire and explosion hazard if heated, subjected to shock, or acidified. They should not be allowed to contact reactive organic matter, including paper and wood. Industrial quantities are packed in fiber drums with polyethylene liners or in metal drums. Laboratory quantities are supplied in glass bottles. For shipment, a yellow oxidizer label is required under DOT regulations.

An important use for sodium bromate *[7789-38-0]*, $NaBrO_3$, is as a neutralizer or oxidizer in certain hair-wave preparations. There also is renewed interest in using mixtures of sodium bromate and sodium bromide for dissolving gold from its ores. The primary use for potassium bromate *[7758-10-2]*, $KBrO_3$, is in flour treatment. Wheat flour containing 5–10 ppm $KBrO_3$ shows better baking characteristics than untreated flour. In analytical chemistry potassium bromate is used as a primary standard and a brominating agent. Barium bromate *[13967-90-3]*, $Ba(BrO_3)_2$, is used in the preparation of rare-earth bromates and as a corrosion inhibitor for low carbon steel.

Perbromic acid *[19445-25-1]*, $HBrO_4$, is a strong acid that is completely dissociated in aqueous solutions. It can be prepared by passing sodium perbromate solution through a cation-exchange resin in hydrogen form. Perbromic acid solutions more concentrated than 6 *M* (55%) are unstable in air apparently undergoing autocatalytic decomposition. Some metal ions, eg, Ag^+ and Ce^{4+}, also catalyze decomposition. Despite the large potential (+1.76 V) of the BrO_4–BrO_3 couple in acidic solution, perbromic acid is a slow oxidizing agent at room temperature. Its oxidizing power increases with concentration and temperature. A 3 *M* solution attacks stainless steel, a 6 *M* solution at 100°C rapidly oxidizes Mn^{2+} to MnO_4 and a 12 *M* solution explodes on contact with cellulose. Perbromic acid can be reduced to bromide with $SnCl_2$. The acid can be used to prepare perbromate salts. Bromate can be oxidized to perbromate in aqueous solutions electrolytically (77), by XeF_2 (77), or by passing fluorine into strongly basic solutions of bromate (78). Sodium perbromate *[33497-30-2]*, $NaBrO_4$, is quite soluble in water, potassium perbromate *[22207-96-1]*, $KBrO_4$, only to the extent of about 0.2 *M* at room temperature. The thermodynamic properties of perbromate and bromate ions have been reported (79).

Organic Compounds

Organic compounds of bromine usually resemble their chlorine analogues but have higher densities and lower vapor pressures. The bromo compounds are more reactive toward alkalies and metals; brominated solvents should generally be kept from contact with active metals such as aluminum. On the other hand, they present less fire hazard: one bromine atom per molecule reduces flammability about as much as two chlorine atoms.

Methyl Bromide. Methyl bromide *[74-83-9]* (bromomethane), CH_3Br, is a colorless liquid or gas with practically no odor. Its physical properties are: mp, 93.7°C; bp, 3.56°C; liquid d^{0}_{4}, 1.730 g/mL; vapor d^{0}_{gas}, 3.974 g/L; n^{20}, 1.4432; vapor pressure at 20°C, 189.3 kPa (1420 mm Hg); viscosity at −20, 0, and 25°C: 0.475, 0.397, and 0.324 mPa·s(=cP), respectively. Heat capacity of the liquid at −13.0°C and the vapor at 25°C, 824 (197), and 448 (107), J/(kg·K) [cal/(kg·K)], respectively; heat of vaporization at 3.6°C, 252 J/g (60.2 cal/g); critical temperature (calculated), 194°C; expansion coefficient, −15 to 3°C, 0.00163/K; dielectric constant at 0°C and 0.001–0.10 MHz, 9.77. The liquid is miscible with most organic solvents and forms a bulky, crystalline hydrate below 4°C. The solubility in water varies with pressure: at normal atmospheric pressure, methyl bromide plus water vapor, the solubility is 1.75 g/100 g solution (20°C).

Methyl bromide slowly hydrolyzes in water, forming methanol and hydrobromic acid. The bromine atom of methyl bromide is an excellent leaving group in nucleophilic substitution reactions and is displaced by a variety of nucleophiles. Thus methyl bromide is useful in a variety of methylation reactions, such as the syntheses of ethers, sulfides, esters, and amines. Tertiary amines are methylated by methyl bromide to form quaternary ammonium bromides, some of which are active as microbicides.

Methyl bromide reacts readily with a number of metals to form organometallic reagents useful as catalysts or for the introduction of a methyl group into a variety of organic or organometallic compounds. Reaction with magnesium gives the well-known Grignard reagent (see GRIGNARD REACTION), usually prepared in an ether solvent. Reaction with lithium in ether forms methyllithium *[917-54-4]*, from which the versatile lithium dimethyl copper *[15681-48-8]* reagent can be made by reaction with anhydrous cuprous iodide *[7681-65-4]*.

$$CH_3Br + 2\,Li \rightarrow CH_3Li + LiBr$$

$$2\,CH_3Li + CuI \rightarrow Li[(CH_3)_2Cu] + LiI$$

Reactions with zinc or aluminum are typically carried out in hydrocarbon solvents. Many of the methylmetal derivatives undergo protonolysis or oxidation very readily, and must be protected from exposure to air or water.

Methyl bromide, when dry (<100 ppm water), is inert toward most materials of construction. Carbon steel is recommended for storage vessels, piping, pumps, valves, and fittings. Copper, brass, nickel, and its alloys are sometimes used. Aluminum, magnesium, zinc, and alloys of these metals should not be used because under some conditions dangerous pyrophoric compounds may be formed. Many nonmetallic materials are also useful for handling methyl bromide, but nylon and polyvinyl chloride should be avoided.

Methyl bromide is nonflammable over a wide range of concentrations in air at atmospheric pressure and offers practically no fire hazard. With an intense source of ignition, flame propagation within a narrow range from 13.5 to 14.5% by volume has been reported. The material has no flash point. Thermal decomposition in a glass vessel begins somewhat above 400°C.

Commercial manufacture of methyl bromide is generally based on the reaction of hydrogen bromide with methanol. For laboratory preparation, the addition of sulfuric acid to sodium bromide and methanol has been used (80). Another method involves the treatment of bromine with a reducing agent, such as phosphorus or sulfur dioxide, to generate hydrogen bromide (81).

Methyl bromide is sold both as the essentially pure compound, 99.5% minimum, with not more than 0.010% water and 0.001% acidity as HBr, and with small amounts of chloropicrin *[76-06-2]*, CCl_3NO_2. During 1992 methyl bromide in tank cars was priced at $1.70/kg. Methyl bromide is supplied in 37,850- and 60,560-L tank cars and in 12,220-L ISO cylinders. Repackagers supply methyl bromide in 0.45 kg or 0.68 kg cans for such applications as fumigating tobacco seed beds. Alone or in formulations, it is classified as a poison, class B, and requires a poison label.

With observance of the proper precautions, methyl bromide may be transported and used safely. Methyl bromide is a colorless and practically odorless gas or liquid having very poor warning properties. Chloropicrin, a slightly oily colorless liquid that has an intensely irritating odor, has excellent warning properties and is sometimes added to methyl bromide to provide a warning odor. Because methyl bromide is normally a gas, the liquid evaporates rapidly and can cause frost-type burns when large amounts evaporate from the skin. Vapor trapped next to the skin can cause severe delayed burns. Methyl bromide is corrosive to the eyes. Inhalation of this chemical can cause dizziness, nausea, vomiting, headache, drowsiness, dimming of vision, and death. Respiratory tract inflammation can occur from breathing methyl bromide. These symptoms can be delayed 2–48 h. Repeated and prolonged exposure to lower concentrations (30–100 ppm) causes severe nervous system effects. Methyl bromide has been shown to be mutagenic in laboratory tests (82).

The time-weighted average limit for daily 8-h exposure to the vapor in air is 5 ppm by volume, or 19 mg/m^3 (67). A full facepiece gas mask with an appropriate canister may be used in areas where the concentration of methyl bromide is known and is no more than 2000 ppm. For unknown or higher concentrations a positive pressure, self-contained breathing apparatus is required. A full facepiece respirator should be worn whenever there is a likelihood of getting methyl bromide in the eyes. No gloves, finger rings, or adhesive bandages should be worn on the hands and no ordinary rubber protective clothing or boots should be worn when handling methyl bromide. If contaminated, clothing should be removed promptly and shoes should be discarded. Wash facilities for eyes and skin should be provided near work areas (82).

The primary use for methyl bromide is in the extermination of insect and rodent pests. Methyl bromide is used in space and structural fumigation except in California. The material is suitable for the fumigation of food commodities such as dried fruits, grain, flour, and nuts, and the facilities in which these foods are processed or stored, as well as for tobacco and many kinds of nursery stock. The usual dosage is 2–4 kg/28 m^3 for 12–24 h. In soil fumigation methyl bromide controls weed seeds, nematodes, wireworms, and soil fungi. The usual dosage is 0.5–1 kg/9 m^2 for 24 h at 16°C and above (82).

Methyl bromide finds use as a methylating agent in the syntheses of agricultural and drug chemicals. It is also used in ionization chambers, for degreasing wool, and for extracting oil from nuts, seeds, and flowers.

Other Bromomethanes. Bromochloromethane *[74-97-5]* (methylene chlorobromide), CH_2BrCl, is a clear, colorless liquid with a characteristic sweet odor and very low freezing point, −88.0°C. Its properties include: bp, 68.1°C; d^{25}_{4}, 1.9229 g/mL; n^{25}_{D}, 1.4808; heat of vaporization at bp, 232 J/g (55.4 cal/g). The liquid is completely miscible with common organic solvents and soluble in water to the extent of about 0.9 g per 100 g at 25°C. Common methods of preparation involve the partial replacement of chloride in methylene chloride *[75-09-2]* (dichloromethane) by reaction with anhydrous aluminum bromide, treatment with bromine and aluminum (83), or by reaction with hydrogen bromide in the presence of an aluminum halide catalyst (84). The principal outlet for bromochloromethane is as a fire-extinguisher fluid; its effectiveness per unit weight suits it for use in aircraft and portable extinguishers. It is also used as an explosion suppression agent and as an intermediate and solvent in the manufacture of pesticides and other products. Its toxicity is also lower than that of many bromine compounds (85). Its price in 1992 was $2.80/kg in bulk.

Dibromomethane *[74-95-3]* (methylene bromide), CH_2Br_2, is a similar liquid, mp −52.7°C, bp 96.9°C, d^{20}_{4} 2.4956 g/mL, n^{20}_{D} 1.5419. Water solubility is 1.17 g/100 g at 15°C. It is prepared by the same methods as bromochloromethane, allowing the reaction to proceed to completion. A laboratory preparation involves removing a bromine from bromoform using sodium arsenite (86). The compound is used as a solvent, as a gauge fluid, and in producing pesticides. Both of these dihalomethanes can be used as dense, readily volatile media for mineral and salt separations.

Tribromomethane *[75-25-2]* (bromoform), $CHBr_3$, is usually sold mixed with up to 3–4% ethanol as a stabilizer. The pure liquid has mp, 7.7°C; bp, 149.5°C; d^{20}_{4}, 2.8912 g/mL; n^{10}_{D} 1.5980 (87). Water solubility is about 0.3 g/100 g at 25°C. Bromoform is prepared from chloroform by the replacement procedures indicated (88). The classical method of preparation involves reaction of acetone and sodium hypobromite; the latter may be generated from sodium hypochlorite and a bromide (89). Uses have been found in syntheses, in pharmacy as a sedative and antitussive, in gauge fluids, and as a dense liquid for separating minerals. Traces of bromoform and bromochloroforms are likely to be present in municipal waters and wastes as a result of chlorination in the presence of naturally occurring bromide ions and humic substances (90). Removal can be accomplished by adsorption on activated charcoal.

Tetrabromomethane *[558-13-4]* (carbon tetrabromide), CBr_4, is a white to brownish powder; mp 90.1°C; bp, 189.5°C; d^{20}_{4}, 3.240 g/mL; $n^{99.5}_{D}$, 1.600 (91). The compound is monoclinic at room temperature and has a transition to cubic at 46.9°C. It is prepared by replacement of chlorine in carbon

tetrachloride using hydrogen bromide and an aluminum halide catalyst (84). It can also be prepared from bromoform (or acetone) and sodium hypobromite containing excess bromine, by an extension of the haloform reaction (92). Carbon tetrabromide is capable of direct addition to olefins; with ethylene it forms 1,1,1,3-tetrabromopropane *[62127-50-8]* (93). It is also light-sensitive. A number of patents have covered possible uses in photography and photo-duplicating systems.

Various bromofluoromethanes have been described and proposed for use as fire extinguishing agents (qv). Two that have been recommended highly for this purpose are dibromo difluoromethane *[75-61-6]*, CBr_2F_2, and bromotrifluoromethane *[75-63-8]*, $CBrF_3$, (94). Bromochlorodifluoromethane *[353-59-3]*, $CBrClF_2$, is another fire extinguishing agent. These and similar substituted methanes are potentially useful for the synthesis of other halo–fluoro compounds.

Ethyl Bromide. Ethyl bromide *[74-96-4]* (bromoethane), CH_3CH_2Br, is a volatile, clear, colorless liquid of mp, 119.3°C; bp, 38.4°C; d^{25}_4, 1.4492 g/mL; n^{25}_D, 1.421 (95). It is completely miscible with most neutral or acidic organic solvents but may react with bases. The solubility in water is ca 0.9 g/100 g at 25°C. Ordinarily, ethyl bromide is prepared by refluxing ethanol with hydrobromic acid, or with an alkali bromide and sulfuric acid (96). The reaction of ethane with sulfur trioxide and potassium bromide at 300–325°C is reported to produce ethyl bromide with a yield of 91% based on ethane consumed (97). Ethyl bromide is used mainly as an ethylating agent in syntheses, particularly of pharmaceuticals. Some has been employed as a solvent or refrigerant, and formerly as a local anesthetic applied as a spray. Its toxicity is markedly lower than that of methyl bromide. Technical-grade (98%) product in truckloads of 208-L (55 gal.) drums was priced in 1992 at $2.80/kg.

Ethylene Dibromide. Ethylene dibromide *[106-93-4]* (ethylene bromide, 1,2-dibromoethane), CH_2BrCH_2Br, is a clear, colorless liquid with a characteristic sweet odor. Its properties include: mp, 9.9°C; bp, 131.4°C; d^{20}_4, 2.1792 g/mL (47); n^{20}_D, 1.5380 (98); vapor pressure, 1.13 (8.5), 15.98 (119.8), and 38.03 kPa (285.2 mm Hg) at 20, 75, and 100°C, respectively; viscosity at 20°C, 1.727 mPa·s(=cP); heat capacity of the solid at 15.3°C, 519 J/(kg·K) (124 cal/(kg·K) and of the liquid at 21.3°C, 724 J/(kg·K) (173 cal/(kg·K); heat of fusion at 9.9°C, 53.4 J/g (12.76 cal/g); heat of vaporization at bp, 191 J/g (45.7 cal/g); heat of transition at −23.6°C, 10.34 J/g (2.47 cal/g); critical temperature, 309.8°C; critical pressure, 7154 kPa (70.6 atm); expansion coefficient at 15–30°C, 0.000958/K (99); dielectric constant at 20.5°C (0.1 MHz), 4.77. The liquid is completely miscible with carbon tetrachloride, benzene, gasoline, ether, and anhydrous alcohols at 25°C and solubility in water at 20°C is 0.404 g/100 g solution.

Ethylene dibromide is nonflammable and under ordinary conditions is quite stable. Slight decomposition may occur on exposure to light. The heat of combustion in an oxygen bomb is 6647 J/g (1589 cal/g). At 340–370°C in a glass vessel, ethylene dibromide decomposes into vinyl bromide and hydrogen bromide. Vinyl bromide is also formed slowly on contact with a warm alkaline solution. Ethylene glycol is produced by high temperature hydrolysis under pressure, and the reaction with zinc in alcohol yields ethylene and zinc bromide. If a mixture of liquid ammonia and ethylene dibromide is allowed to reach room temperature, an explosion may result with formation of ethylenediamine and higher homologues.

In the manufacture of ethylene dibromide, gaseous ethylene is brought into contact with bromine by various methods, allowing for dissipation of the heat of reaction (100–102). Free acids are neutralized and the product may be fractionally distilled for purification. Typical specifications call for a clear liquid with 99.5% purity min; sp gr (25/25°C), 2.170–2.180; boiling range, 130.4–132.4°C; APHA color, 200 max; water, 200 ppm max; acidity as HCl, 0.0004 wt% max; and nonvolatile matter, 0.0050 wt% max.

Ethylene dibromide is a suspected human carcinogen and worker exposure by all routes should be carefully controlled to levels as low as reasonably achievable (67). Ethylene dibromide causes severe blistering of the skin if contact is prolonged. Eye contact with the liquid will cause pain, irritation, and temporary impairment of vision. Recommended safety equipment includes safety goggles, a NIOSH approved canister-type gas mask for organic vapors, neoprene gloves, and neoprene overshoes. In case of contact with ethylene dibromide, contaminated clothing and shoes should be removed and eyes or skin washed with plenty of water for at least 15 minutes. Contaminated clothes should be washed before reuse and contaminated shoes should be discarded.

Ethylene dibromide is one of the lowest cost organic compounds of bromine, priced during 1992 at $1.26/kg in tank cars. This compound has found its primary use as an exhaust system scavenger in gasolines containing lead antiknocks and is still used for this purpose in countries where leaded gasolines are sold. Ethylene bromine once found considerable use as an agricultural fumigant but this use in the United States is now prohibited. Other uses are in the manufacturing of dyes, pharmaceuticals, polymers, and other chemicals. It is a general solvent for resins, waxes, gums, and dyes.

Chemical Intermediates and Reagents. Table 1 lists some chemical intermediates and synthesis reagents containing bromine. The references cited in the table generally give a method of synthesis and often some physical properties. Other physical properties are also available (194–196).

Table 1. Organobromine Compounds

Compound	CAS Registry Number	Molecular formula	Mp, °C	Bp, °C[a]	d^{20}_4[b]	n^{20}_D[b]	Uses[c] and miscellaneous properties	References
acetobromglucose	*[572-09-8]*	$C_{14}H_{19}BrO_9$	88–89				S	103
acetyl bromide	*[506-96-7]*	CH_3COBr	96	76	1.6625[1]	1.45376[1]	S, lachrimator	104
acetylene dibromide (*cis* and *trans*)	*[540-49-8]*	BrCH=CHBr		110[75,4]	2.246	1.5405	S, corrosive lachrimator	105
acetylene tetrabromide	*[79-27-6]*	$CHBr_2CHBr_2$	0.1	151	2.9638	1.6380	S, solvent, dense fluid, toxic mutagen	106,107
allyl bromide	*[106-95-6]*	$CH_2=CHCH_2Br$	119	71.3	1.398	1.46545	S, irritating vapor, toxic	108
d-amyl bromide	*[534-00-9]*	$CH_3CH_2CH(CH_3)CH_2Br$		121–122	1.223	1.4444	S, optically active, irritant	109
n-amyl bromide	*[110-53-2]*	$CH_3(CH_2)_3CH_2Br$	95	130	1.218	1.4436	S, irritant	110
tert-amyl bromide	*[507-36-8]*	$(CH_3)_2CBrCH_2CH_3$		107.4	1.182	1.4423	S	111
benzyl bromide	*[100-39-0]*	$C_6H_5CH_2Br$	3.9	198–199	1.438	1.5750	S, corrosive lachrimator	112
1,2-bis(bromomethyl)benzene	*[91-13-4]*	$C_6H_4(CH_2Br)_2$	93–94				S	113
1,4-bis(bromomethyl)benzene	*[623-24-5]*	$C_6H_4(CH_2Br)_2$	143.5	245			S	114
bromal (tribromoacetaldehyde)	*[115-17-3]*	Br_3CCHO		174	2.665	1.5860	S, corrosive lachrimator	115
bromal hydrate	*[507-42-6]*	$Br_3CCH(OH)_2$	53.5		2.5662[40]		S	116
N-bromoacetamide	*[79-15-2]*	$CH_3CONHBr$	102–105				brominating agent, oxidizes 1° and 2° alcohols, irritant	117
bromoacetic acid	*[79-08-3]*	$BrCH_2COOH$	50	208	1.93		S, corrosive lachrimator	118
bromoacetone	*[598-31-2]*	CH_3COCH_2Br	36.5	137	1.634[23]	1.4697	S, violent lachrimator	119,120

p-bromoacetophenone	*[99-90-1]*	$BrC_6H_4COCH_3$	54	255	1.647		S, irritant	121
ω-bromoacetophenone	*[70-11-1]*	$C_6H_5COCH_2Br$	50	135^{18}	1.647		S, corrosive lachrimator	122
p-bromoaniline	*[106-40-1]*	$H_2NC_6H_4Br$	66.4		1.4970^{100}		prep of azo dyes, dihydroquinazolines, toxic	123
5-bromoanthranilic acid	*[5794-88-7]*	$BrC_6H_3(NH_2)COOH$	218–219				detn of cobalt, copper, nickel, and zinc; irritant	124
bromobenzene	*[108-86-1]*	C_6H_5Br	30.8	156.2	1.4952	1.5602	S, solvent	125
p-bromobenzenesulfonyl chloride	*[98-58-8]*	$BrC_6H_4SO_2Cl$	74.5	153^{15}			identification of amines, corrosive, moisture-sensitive	126
p-bromobenzoic acid	*[586-76-5]*	BrC_6H_4COOH	254.5		1.894		S, detection of strontium, irritant	127
p-bromobenzyl bromide	*[589-15-1]*	$BrC_6H_4CH_2Br$	62–64	$115–124^{12}$			identification of aromatic carboxylic acids, corrosive lachrimator	128
p-bromobenzyl chloride	*[589-17-3]*	$BrC_6H_4CH_2Cl$	40–41	$136–139^{27}$			S, irritant	129
p-bromobenzyl chloroformate	*[5798-78-7]*	$BrC_6H_4CH_2OCOCl$					prep amino acids and peptides by carbobenzyloxy method	130
2-bromo-4-*tert*-butylphenol	*[2198-66-5]*	$(CH_3)_3CC_6H_3(OH)Br$	< 20	120^{07}	1.334^{25}	1.550^{25}	S	
α-bromobutyric acid	*[80-58-0]*	$CH_3CH_2CHBrCOOH$	4	$127–128^{25}$	1.567	1.4720	S, corrosive, toxic	131
(±)-α-bromo-*n*-caproic acid	*[616-05-7]*	$CH_3(CH_2)_3CHBrCOOH$	4	240	1.628	1.5030	S, corrosive lachrimator	132
p-bromochlorobenzene	*[106-39-8]*	BrC_6H_4Cl	67.4	196			S, irritant	
bromodichloromethane	*[75-27-4]*	$CHBrCl_2$	57.1	90.1	1.9945	1.4985	S, solvent, cancer suspect agent, toxic	133
2-bromo-*p*-cymene	*[4478-10-8]*	$Br(CH_3)C_6H_3CH(CH_3)_2$	< 20	234.3	1.269^{17}	1.535^{2}	S	134
2-bromodiphenyl	*[2052-07-5]*	$C_6H_5C_6H_4Br$	< 20	296–298	1.2175^{2}		S	135
4-bromodiphenyl	*[92-66-0]*	$C_6H_5C_6H_4Br$	89.5–90	310–311			S	136
α-bromoisobutyric acid	*[2052-01-9]*	$(CH_3)_2CBrCOOH$	48–49	198–200	1.5225		S, corrosive	137
α-bromoisovaleric acid	*[565-74-2]*	$(CH_3)_2CHCHBrCOOH$	44	$124–126^{15}$	1.459		S, corrosive lachrimator	137
β-bromoisovaleric acid	*[5798-88-9]*	$(CH_3)_2CBrCH_2COOH$	73–74				S, corrosive	138
p-bromomandelic acid	*[6940-50-7]*	$BrC_6H_4CHOHCOOH$	118–120				analytical reagent for zirconium, irritant	139
1-bromonaphthalene	*[90-11-9]*	$C_{10}H_7Br$	6.2	281.1	1.4875	1.6582	S	140
2-bromonaphthalene	*[580-13-2]*	$C_{10}H_7Br$	59	287–292	1.605^{0}	1.6382^{0}	S	141
p-bromophenacyl bromide	*[99-73-0]*	$BrC_6H_4COCH_2Br$	109–110				identification of carboxylic acids, corrosive lachrimator	142
m-bromophenol	*[591-20-8]*	BrC_6H_4OH	33	236.5			S, irritant	143
o-bromophenol	*[95-56-7]*	BrC_6H_4OH	5.6	194–195	1.4924	1.5890	S, irritant	144
p-bromophenol	*[106-41-2]*	BrC_6H_4OH	66.4	238	1.840^{15}	1.5875^{80}	S, irritant	144
p-bromophenylhydrazine	*[589-21-9]*	$BrC_6H_4NHNH_2$	108–109				S, irritant	145
p-bromophenyl isocyanate	*[2493-02-9]*	$BrC_6H_4N{=}C{=}O$	42–44	158^{14}			S, prep bromophenyl urea and urethane deriv, lachrimator, moisture-sensitive	146
β-bromopropionic acid	*[590-92-1]*	$BrCH_2CH_2COOH$	62.5		1.480		S	147
3-bromopyridine	*[626-55-1]*	BrC_5H_4N		173–174	1.632^{10}	1.566^{25}	S, highly toxic, irritant	148
5-bromosalicyclic acid	*[89-55-4]*	$Br(OH)C_6H_3COOH$	166				S, irritant	149
(±)-bromosuccinic acid	*[923-06-8]*	$HOOCCH_2CHBrCOOH$	165		2.07		S, irritant	150
N-bromosuccinimide	*[128-08-5]*	$C_4H_4BrNO_2$	180–183		2.098		brominating olefins, oxidizing alcohols to aldehydes and ketones, converting aldehydes to acid bromides	151,152
2-bromothiophene	*[1003-09-4]*	BrC_4H_3S		149–151	1.649^{23}		S	153
m-bromotoluene	*[591-17-3]*	$BrC_6H_4CH_3$	39.8	183.7	1.4099	1.5510	S, irritant	154
o-bromotoluene	*[95-46-5]*	$BrC_6H_4CH_3$	27.8	181.7	1.4232	1.5550	S, irritant	155
p-bromotoluene	*[106-38-7]*	$BrC_6H_4CH_3$	28.5	184.3	1.3995	1.5477	S, irritant	156
n-butyl bromide	*[109-65-9]*	$CH_3(CH_2)_3Br$	112	101.3	1.276	1.4390	S, flammable liquid, irritant	157
sec-butyl bromide	*[78-76-2]*	$CH_3CH_2CHBrCH_3$	112	91.2	1.255	1.4369	S, flammable liquid, irritant	158

tert-butyl bromide	*[507-19-7]*	$(CH_3)_3CBr$	16.3	73.3	1.189	1.4279	S, flammable liquid	159
(±)-α-butylene dibromide	*[533-98-2]*	$CH_3CH_2CHBrCH_2Br$	65	166	1.7946	1.5144	S, irritant	160
cetyldimethylethylammonium bromide	*[124-03-8]*	$[C_{1}H_{33}N(CH_3)_2C_2H_5]^+Br$	190				laboratory reagent, toxic, irritant	161
p-chlorophenacyl bromide	*[536-38-9]*	$ClC_6H_4COCH_2Br$	96–96.5	135^{18}	1.647		prep quat salts of methenamine, chlorophenol glyoximes, corrosive lachrimator	162
cyanogen bromide	*[506-68-3]*	$BrC{\equiv}N$	52	61–62	2.015		S, highly toxic, moisture-sensitive	163
cyclohexyl bromide	*[108-85-0]*	$C_6H_{11}Br$	56.5	166.2	1.3359	1.4957	S	164
9,10-dibromoanthracene	*[523-27-3]*	$C_{14}H_8Br_2$	226				S	165
o-dibromobenzene	*[583-53-9]*	BrC_6H_4Br	1.8	225	1.965	1.6081	S, solvent, irritant	
p-dibromobenzene	*[106-37-6]*	BrC_6H_4Br	87.3	220.4	1.841	1.5743^{99}	S, irritant	166
α,α′-dibromo-*d*-camphor	*[514-12-5]*	$C_{10}H_{14}Br_2O$	61		1.854		S	167
4,4′-dibromodiphenyl	*[92-86-4]*	$BrC_6H_4C_6H_4Br$	163–164	355–360	1.897		S, irritant	168
dibromogallic acid	*[602-92-6]*	$Br_2C_6(OH)_3COOH$	150				S	169
2,3-dibromopropene	*[513-31-5]*	$BrCH_2CBr{=}CH_2$		140–143	1.9336	1.5157	S, lachrimator	170
2,6-dibromoquinone-4-chlorimide	*[537-45-1]*	$C_6H_2Br_2ClNO$	83				reagent for phenol and phosphatases	171
3,5-dibromosalicylic acid	*[3147-55-5]*	$Br_2C_6H_2(OH)COOH$	226–228				S, irritant	172
2,3-dibromosuccinic acid	*[526-78-3]*	$HOOCCHBrCHBrCOOH$	167				S, corrosive	173
diphenylbromomethane	*[776-74-9]*	$(C_6H_5)_2CHBr$	45	193^{35}	1.491^{13}		S	174
ethyl bromoacetate	*[105-36-2]*	$CH_2BrCOOC_2H_5$		159	1.480^{25}	1.451	S, corrosive lachrimator	175
ethyl α-bromopropionate	*[535-11-5]*	$CH_3CHBrCOOC_2H_5$		159–160	1.394	1.4460	S, lachrimator	176
ethylene bromohydrin	*[540-51-2]*	$BrCH_2CH_2OH$		$56–57^{20}$	1.7629	1.4936	S, highly toxic, corrosive	177
ethylene chlorobromide	*[107-04-0]*	CH_2ClCH_2Br	16.5	106.8	1.7392	1.4917	S, solvent, toxic irritant	178
isoamyl bromide	*[107-82-4]*	$(CH_3)_2CHCH_2CH_2Br$	112	120–121	1.261	1.4409	S, flammable liquid, irritant	179
isobutyl bromide	*[78-77-3]*	$(CH_3)_2CHCH_2Br$	119	91.5	1.260	1.4350	S, cancer suspect agent, flammable liquid	180
isopropyl bromide	*[75-26-3]*	$(CH_3)_2CHBr$	89	59	1.310	1.4251	S, flammable liquid, irritant	180
lauryl bromide	*[143-15-7]*	$CH_3(CH_2)_{10}CH_2Br$	(11)–(9)	134–135	1.038	1.4580	S, irritant	181
myristyltrimethylammonium bromide	*[1119-97-7]*	$[C_{14}H_{29}N(CH_3)_3]^+Br$	245–250				laboratory reagent, corrosive, hydroscopic	182
n-octyl bromide	*[111-83-1]*	$CH_3(CH_2)_6CH_2Br$	55	201	1.118	1.4518	S, irritant	183
(±)-*sec*-octyl bromide	*[557-35-7]*	$CH_3CHBr(CH_2)_5CH_3$		66	1.0878^{25}	1.4500	S, irritant	184
propyl bromide	*[106-94-5]*	$CH_3CH_2CH_2Br$	110	71	1.353	1.4341	S, flammable liquid, irritant	185
(±)-propylene dibromide	*[78-75-1]*	$CH_3CHBrCH_2Br$	55	140–142	1.933	1.5203	S, irritant	
pyridinium bromide perbromide	*[39416-48-3]*	$C_5H_6Br_3N$					used in small-scale brominations for its convenience, corrosive lachrimator	186
tribromoacetic acid	*[75-96-7]*	CBr_3COOH	130–133	245			polymerization catalyst, brominating agent, corrosive	187,188
2,4,6-tribromoaniline	*[147-82-0]*	$Br_3C_6H_2NH_2$	120–122	300	2.35		S, irritant	189
2,4,6-tribromophenol	*[118-79-6]*	$Br_3C_6H_2OH$	95–96	$282–290^{74}$	2.55		S, irritant	190
1,2,3-tribromopropane	*[96-11-7]*	$CH_2BrCHBrCH_2Br$	16	220	2.4076^{25}	1.5835^{25}	S, irritant	191
trimethylene bromide	*[109-64-8]*	$BrCH_2CH_2CH_2Br$	34	167	1.9822	1.5232	S, irritant	192
tropylium bromide	*[5376-03-4]*	$[C_7H_7^+Br^-]$	203				S	193

[a] At 101 kPa unless otherwise indicated by superscript; pressure in kPa. To convert kPa to mm Hg, multiply by 7.5.

[b] At 20°C unless otherwise indicated by superscript; temperature in °C.

[c] Where S denotes use in syntheses.

Uses

Dyes and Indicators. The effects of bromine in dye or indicator molecules, in place of hydrogen, include a shift of light absorption to longer wavelengths, increased dissociation of phenolic hydroxyl groups, and lower solubility (see DYES AND DYE INTERMEDIATES). The first two effects probably result from increased polarization caused by bromine's electronegativity compared to that of hydrogen.

Both dibromoindigo *[19201-53-7]*, $C_{16}H_8Br_2N_2O_2$, and tetrabromoindigo *[2475-31-2]*, $C_{16}H_4Br_4N_2O_2$, are brighter in color and have better covering power and light stability than indigo. Ciba Bordeaux B *[6371-14-8]*, $C_{16}H_4Br_2O_2S_2$, is a red dye obtained by brominating thioindigo.

Among anthraquinone dyes (see DYES, ANTHRAQUINONE), Acid Blue 78 *[6424-75-5]*, $C_{21}H_{15}BrN_2O_5S \cdot Na$, or Alizarin Pure Blue B, is a wool dye. Bromamine acid *[116-81-4]* (1-amino-4-bromoanthraquinone-2-sulfonic acid), $C_{14}H_8BrNO_5S$, is a useful dye intermediate. A number of bromo anthraquinone, pyrathrone, and benzanthrone dyes are known.

Other bromine-containing dye intermediates include 6-bromo-2,4-dinitroaniline *[1817-73-8]*, $C_6H_4BrN_3O_4$, and 5,7-dibromoisatin *[6374-91-0]*, $C_8H_3Br_2NO_2$. Bromodinitroaniline is used in making azo dyes and dibromoisatin is used in making Alizarin Indigos B, 3R, and G.

Eosin *[15086-94-9]* (tetrabromofluorescein), $C_{20}H_8Br_4O_5$, made by the bromination of fluorescein, is both a dye and an adsorption indicator. Eosin Y *[17372-87-1]*, $C_{20}H_6Br_4O_5 \cdot 2Na$, the disodium salt, is a biological stain. 4′,5′-Dibromofluorescein *[596-03-2]*, $C_{20}H_{10}Br_2O_5$, is used in D & C Orange No. 5 permitted for use in lipsticks, mouthwashes, and dentrifices (qv). Eosine I Bluish *[548-24-3]*, $C_{20}H_6Br_2N_2O_9 \cdot 2Na$, is used in dyeing wool, cotton (qv), and paper; and in histology as a stain. Eosine Yellowish-(YS) *[17372-87-1]*, $C_{20}H_6Br_4O_5 \cdot 2Na$, is used in cosmetics (qv) and drugs; in dyeing wool (qv), silk (qv), and paper (qv); and in red inks (qv). Methyl green *[14855-76-6]*, $C_{27}H_{35}N_3 \cdot Br \cdot Cl$, is used in dyeing and printing textiles (qv) and as a biological stain.

Bromine-containing indicators are listed in Table 2.

Table 2. Bromine-Containing Indicators

Indicator	CAS Registry Number	Molecular formula	pH	Color	pH	Color
bromcresol green	*[76-60-8]*	$C_{21}H_{14}Br_4O_5S$	3.8	yellow	5.4	blue-green
bromcresol purple	*[115-40-2]*	$C_{21}H_{16}Br_2O_5S$	5.2	yellow	6.8	purple
bromphenol blue	*[115-39-9]*	$C_{19}H_{10}Br_4O_5S$	3.0	yellow	4.6	purple
bromthymol blue	*[76-59-5]*	$C_{27}H_{28}Br_2O_5S$	6.0	yellow	7.6	purple

Flame Retardants. Bromine compounds make up an important segment of the market for flame retardants used in polymers. Additive flame retardants are added to polymers during processing; reactive flame retardants react chemically to become part of the polymer chain itself. In addition to the compounds listed in Table 3, a number of proprietary mixtures and phosphorus–bromine-containing flame retardants are also sold (see FLAME RETARDANTS, HALOGENATED, FLAME RETARDANTS).

Table 3. Commercial Brominated Flame Retardants

Compound	CAS Registry Number	Molecular formula	Compound	CAS Registry Number	Molecular formula
Additive flame retardants			*Reactive flame retardants*		
pentabromodiphenyl oxide	*[32534-81-9]*	$C_{12}H_5Br_5O$	tetrabromophthalic anhydride	*[632-79-1]*	$C_8Br_4O_3$
octabromodiphenyl oxide	*[32536-52-0]*	$C_{12}H_2Br_8O$	disodium salt of tetrabromophthalate diester ether diol[a] of tetrabromophthalic anhydride	*[77098-07-8]*	
decabromodiphenyl oxide	*[1163-19-5]*	$C_{12}Br_{10}O$	dibromoneopentyl glycol	*[3296-90-0]*	$C_5H_{10}Br_2O_2$
tetradecabromodiphenoxy-benzene	*[58965-66-5]*	$C_{18}Br_{14}O_2$	tribromoneopentyl alcohol	*[1522-92-5]*	$C_5H_9Br_3O$
dibromoethyldibromocyclo-hexane	*[3322-93-8]*	$C_8H_{12}Br_4$	tetrabromodipentaerythritol	*[109678-33-3]*	$C_{10}H_{18}Br_4O_3$
hexabromocyclododecane	*[3194-55-6]*	$C_{12}H_{18}Br_6$	tetrabromobisphenol A	*[79-94-7]*	$C_{15}H_{12}Br_4O_2$
ethylenebistetrabromo-phthalimide	*[32588-76-4]*	$C_{18}H_4Br_8N_2O_4$	tetrabromobisphenol A-bis (2-hydroxyethyl ether)		
ethylenebisdibromonorbor-nanedicarboximide	*[41291-34-3]*	$C_{20}H_{20}Br_4N_2O_4$	tetrabromobisphenol A-bis (2,3-dibromopropyl ether)		
bis(2-ethylhexyl)tetrabromo-phthalate	*[26040-51-7]*	$C_{24}H_{34}Br_4O_4$	tetrabromobisphenol A-bis (allyl ether)		
bis(tribromophenoxy)ethane			2,4-dibromophenol	*[615-58-7]*	$C_6H_4Br_2O$
poly(dibromostyrene)	*[62354-98-7]*	$(C_8H_6Br_2)_x$	2,4,6-tribromophenol	*[118-79-6]*	$C_6H_3Br_3O$
poly(dibromophenylene oxide)			vinyl bromide	*[593-60-2]*	C_2H_3Br
			tribromophenyl allyl ether	*[26762-91-4]*	$C_9H_7Br_3O$
			dibromostyrene	*[31780-26-4]*	$C_8H_6Br_2$

[a] Diethylene glycol propylene glycol ester.

Pesticides. Bromine-containing pesticides are given in Table 4.

Table 4. Organobromines Used as Pesticides

Compound	CAS Registry Number	Molecular formula	Compound	CAS Registry Number	Molecular formula
Acaricide			*Insecticide and acaricide*		
bromopropylate	*[18181-80-1]*	$C_{17}H_{16}Br_2O_3$	bromophos	*[2104-96-3]*	$C_8H_8BrCl_2O_3PS$
			naled	*[300-76-5]*	$C_4H_7Br_2Cl_2O_4P$
Algaecide			*Insect fumigant*		
ethyldimethyl-9-octadecenyl-ammonium bromide	*[6458-13-5]*	$C_{22}H_{46}N \cdot Br$	methyl bromide	*[74-83-9]*	CH_3Br
Fungicide			*Nematocide*		
3,4,5,6-tetrabromo-*o*-cresol	*[576-55-6]*	$C_7H_4Br_4O$	1,2,3-tribromopropane	*[96-11-7]*	$C_3H_5Br_3$
Herbicide			*Rodenticide*		
bromacil	*[314-40-9]*	$C_9H_{13}BrN_2O_2$	bromadiolone	*[28772-56-7]*	$C_{30}H_{23}BrO_4$
bromoxynil	*[1689-84-5]*	$C_7H_3Br_2NO$	brodifacoum	*[56073-10-0]*	$C_{31}H_{23}BrO_3$
diquat dibromide	*[85-00-7]*	$C_{12}H_{12}N_2 \cdot 2Br$	bromethalin	*[9001-00-7]*	

isocil	*[314-42-1]*	$C_8H_{11}BrN_2O_2$
metobromuron	*[3060-89-7]*	$C_9H_{11}BrN_2O_2$
Insecticide		
deltamethrin	*[52918-63-5]*	$C_{22}H_{19}Br_2NO_3$
leptophos	*[21609-90-5]*	$C_{13}H_{10}BrCl_2O_2PS$

Pharmaceuticals. Numerous bromine compounds are pharmaceuticals (qv) (194). Some are listed in Table 5.

Table 5. Organobromines Used in Pharmaceuticals

Compound	CAS Registry Number	Molecular formula
Adrenergic (opthalmic)		
hydroxyamphetamine hydrobromide[a]	*[306-21-8]*	$C_{9}H_{13}NO \cdot HBr$
Analgesic, narcotic		
codeine hydrobromide	*[125-25-7]*	$C_{18}H_{21}NO_3 \cdot HBr$
codeine methyl bromide	*[125-27-9]*	$C_{19}H_{24}NO_3 \cdot Br$
morphine hydrobromide	*[630-81-9]*	$C_{17}H_{19}NO_3 \cdot HBr$
morphine methylbromide	*[125-23-5]*	$C_{18}H_{22}NO_3 \cdot Br$
phenazocine hydrobromide[a]	*[1239-04-9]*	$C_{22}H_{27}NO \cdot HBr$
Anesthetic, inhalation		
halopropane	*[679-84-5]*	$C_3H_3BrF_4$
halothane[a]	*[151-67-7]*	$C_2HBrClF_3$
teflurane	*[124-72-1]*	C_2HBrF_4
tribromoethanol	*[75-80-9]*	$C_2H_3Br_3O$
Antiadrenergic and cardiac depressant		
bretylium tosylate	*[61-75-6]*	$C_{11}H_{17}BrN \cdot xC_7H_7O_3S$
Antibacterial		
brodimoprim	*[56518-41-3]*	$C_{13}H_{15}BrN_4O_2$
5-bromosalicylhydroxamic acid	*[5798-94-7]*	$C_7H_6BrNO_3$
3,5-dibromosalicylaldehyde	*[90-59-5]*	$C_7H_4Br_2O_2$
merbromin	*[129-16-8]*	$C_{20}H_{10}Br_2HgO_6 \cdot 2Na$
sulfabromomethazine	*[116-45-0]*	$C_{12}H_{13}BrN_4O_2S$
piperilate ethyl bromide		
propantheline bromide[a]	*[50-34-0]*	$C_{23}H_{30}NO_3 \cdot Br$
propyromazine	*[145-54-0]*	$C_{10}H_{23}N_2OS \cdot Br$
Anticoagulant		
bromindione	*[1146-98-1]*	$C_{15}H_9BrO_2$
Anticonvulsant		
cinromide	*[58473-74-8]*	$C_{11}H_{12}BrNO$
narcobarbital	*[125-55-3]*	$C_{11}H_{15}BrN_2O_3$
Antidepressant		
zimeldine	*[56775-88-3]*	$C_{11}H_{17}BrN_2$
Antiemetic		
bromopride	*[4093-35-0]*	$C_{14}H_{22}BrN_3O_2$
Antifungal agent		
bromosalicylchloranilide	*[3679-64-9]*	$C_{13}H_9BrClNO_2$
2,4,6-tribromo-*m*-cresol	*[4619-74-3]*	$C_7H_5Br_3O$
Antihistaminic		
bromodiphenhydramine	*[118-23-0]*	$C_{17}H_{20}BrNO$
brompheniramine	*[86-22-6]*	$C_{16}H_{19}BrN_2$
brompheniramine (*d*-form)	*[132-21-8]*	$C_{16}H_{19}BrN_2$
p-bromtripelennamine	*[531-09-09]*	$C_{16}H_{20}BrN_3$
embramine	*[3565-72-8]*	$C_{18}H_{22}BrNO$
pyrilamine	*[91-84-9]*	$C_{17}H_{23}N_3O$
Anticholinergic		
adiphenine hydrochloride	*[50-42-0]*	$C_{20}H_{25}NO_2 \cdot HCl$
ambutonium bromide	*[115-51-5]*	$C_{20}H_{27}N_2O \cdot Br$
anisotropine methylbromide	*[80-50-2]*	$C_{17}H_{32}NO_2 \cdot Br$
benzilonium bromide	*[1050-48-2]*	$C_{22}H_{28}NO_3 \cdot Br$
clidinium bromide[a]	*[3485-62-9]*	$C_{22}H_{26}NO_3 \cdot Br$
endobenzyline bromide	*[52080-56-5]*	$C_{20}H_{28}NO_3 \cdot Br$
glycopyrrolate[a]	*[596-51-0]*	$C_{19}H_{28}NO_3 \cdot Br$
heteronium bromide	*[7247-57-6]*	$C_{18}H_{22}NO_3S \cdot Br$
hyoscyamine hydrobromide[a]	*[306-03-6]*	$C_{17}H_{23}NO_3 \cdot HBr$
mepenzolate bromide	*[76-90-4]*	$C_{21}H_{26}NO_3 \cdot Br$
methantheline bromide[a]	*[53-46-3]*	$C_{21}H_{26}NO_3 \cdot Br$
methscopolamine bromide[a]	*[155-41-9]*	$C_{18}H_{24}NO_4 \cdot Br$
oxyphenonium bromide	*[50-10-2]*	$C_{21}H_{34}NO_3 \cdot Br$
penthienate bromide[a]	*[60-44-6]*	$C_{18}H_{30}NO_3S \cdot Br$

pipenzolate bromide	*[125-51-9]*	$C_{22}H_{28}NO_3 \cdot Br$
scopolamine hydrobromide[a]	*[114-49-8]*	$C_{17}H_{21}NO_4 \cdot HBr$
thihexinol methylbromide[a]	*[7219-91-2]*	$C_{18}H_2\ NOS_2 \cdot Br$
timepidium bromide	*[35035-05-3]*	$C_{17}H_{22}NOS_2 \cdot Br$
valethamate bromide[a]	*[90-22-2]*	$C_{19}H_{32}NO_2 \cdot Br$
Analgesic		
p-bromoacetanilide	*[103-88-8]*	C_8H_8BrNO
5-bromosalicyclic acid acetate	*[1503-53-3]*	$C_9H_7BrO_4$
Anticholinergic (ophthalmic)		
homatropine hydrobromide[a]	*[51-56-9]*	$C_1\ H_{21}NO_3 \cdot HBr$
homatropine methylbromide	*[80-49-9]*	$C_{17}H_{24}NO_3 \cdot Br$
Anticholinergic and antispasmodic		
butropium bromide	*[29025-14-7]*	$C_{28}H_{38}NO_4 \cdot Br$
fentonium bromide	*[5868-06-4]*	$C_{31}H_{34}NO_4 \cdot Br$
Antihypertensive		
azamethonium bromide	*[306-53-6]*	$C_{13}H_{33}N_3 \cdot 2Br$
hexamethonium bromide	*[55-97-0]*	$C_{12}H_{30}N_2 \cdot 2Br$
pentamethonium bromide	*[541-20-8]*	$C_{11}H_{28}N_2 \cdot 2Br$
Antiinfective		
bismuth tribromophenate	*[5175-83-7]*	$C\ H_3Br_3O \cdot 1\ 3Bi$
domiphen bromide	*[538-71-6]*	$C_{22}H_{40}NO \cdot Br$
Antiinflammatory		
bromosaligenin	*[2316-64-5]*	$C_7H_7BrO_2$
halopredone acetate	*[57781-14-3]*	$C_{25}H_{29}BrF_2O_7$
Antimalarial		
quinine dihydrobromide	*[549-47-3]*	$C_{20}H_{24}N_2O_3 \cdot 2HBr$
quinine hydrobromide	*[549-49-5]*	$C_{20}H_{24}N_2O_2 \cdot HBr$
Antineoplastic		
mitobronitol	*[488-41-5]*	$C\ H_{12}Br_2O_4$
mitolactol	*[10318-26-0]*	$C\ H_{12}Br_2O_4$
pipobroman[a]	*[54-91-1]*	$C_{10}H_1\ Br_2N_2O_2$
Antipsychotic		
bromperidol	*[10457-90-6]*	$C_{21}H_{23}BrFNO_2$
Antiseptic		
amantanium bromide	*[58158-77-3]*	$C_{25}H_4\ NO_2 \cdot Br$
bibrocathol	*[6915-57-7]*	$C\ HBiBr_4O_3$
bronopol	*[52-51-7]*	$C_3H\ BrNO_4$
broxyquinoline	*[521-74-4]*	$C_9H_5Br_2NO$
cethexonium bromide	*[1794-74-7]*	$C_{24}H_{50}NO \cdot Br$
Antiseptic		
cetrimonium bromide	*[57-09-0]*	$C_{19}H_{42}N \cdot Br$
cetyldimethylethylammonium bromide	*[124-03-8]*	$C_{20}H_{44}N \cdot Br$
dibromopropamidine	*[496-00-4]*	$C_{17}H_{18}Br_2N_4O_2$
dibromsalicil	*[523-88-6]*	$C_{14}H_8Br_2O_4$
Antispasmodic		
N-butylscopolammonium bromide	*[149-64-4]*	$C_{21}H_{30}NO_4 \cdot Br$
cimetropium bromide	*[51598-60-8]*	$C_{21}H_{28}NO_4 \cdot Br$
coniine hydrobromide	*[637-49-0]*	$C_8H_{17}N \cdot HBr$
diponium bromide	*[2001-81-2]*	$C_{20}H_{38}NO_2 \cdot Br$
emepronium bromide	*[3614-30-0]*	$C_{20}H_{28}N \cdot Br$
fenpiverinium bromide	*[125-60-0]*	$C_{22}H_{29}N_2O \cdot Br$
prifinium bromide	*[4630-95-9]*	$C_{22}H_{28}N \cdot Br$
spasmolytol	*[25333-96-4]*	$C_{14}H_{21}Br_2NO_2$
tiquizium bromide	*[71731-58-3]*	$C_{19}H_{24}NS_2 \cdot Br$
tropenzile	*[53834-53-0]*	$C_{23}H_{27}NO_4$
Antitussive		
bibenzonium bromide	*[15585-70-3]*	$C_{19}H_2\ NO \cdot Br$
dextromethorphan hydrobromide[a]	*[125-69-9]*	$C_{18}H_{25}NO \cdot HBr$
Anxiolytic		
bromazepam	*[1812-30-2]*	$C_{14}N_{10}BrN_3O$
magnesium glutamate hydrobromide		
metaclazepam	*[84031-17-4]*	$C_{18}H_{18}BrClN_2O$
Disinfectant		
3,5-dibromo-4-hydroxybenzenesulfonic acid	*[4232-99-9]*	$C\ H_4Br_2O_4S$
fluorosalan	*[4776-06-1]*	$C_{14}H_8Br_2F_3NO_2$
myristyltrimethylammonium bromide	*[1119-97-7]*	$C_{17}H_{38}N \cdot Br$
Diuretic		
pamabrom	*[606-04-2]*	$C_7H_7BrN_4O_2 \cdot C_4H_{11}NO$
Emetic		
apomorphine methylbromide	*[602-81-3]*	$C_{18}H_{20}NO_2 \cdot Br$
cephaeline dihydrobromide[a]	*[6014-81-9]*	$C_{28}H_{38}N_2O_4 \cdot 2BrH \cdot 7H_2O$
Enzyme inhibitor (prolactin) and antiparkinsonian agent		

bromocriptine[a]	*[25614-03-3]*	$C_{32}H_{40}BrN_5O_5$
Estrogen used in dermatology		
broparoestrol	*[479-68-5]*	$C_{22}H_{19}Br$
Expectorant		
ambroxol	*[18683-91-5]*	$C_{13}H_{18}Br_2N_2O$
bromhexine	*[3572-43-8]*	$C_{14}H_{20}Br_2N_2$
Ganglion blocking agent		
tetraethylammonium bromide	*[71-91-0]*	$C_8H_{20}N \cdot Br$
Bronchodilator		
flutropium bromide	*[63516-07-4]*	$C_{24}H_{29}FNO_3 \cdot Br$
oxitropium bromide	*[30286-75-0]*	$C_{19}H_{2}\ NO_4 \cdot Br$
rimiterol	*[32953-89-2]*	$C_{12}H_{17}NO_3$
Bronchodilator and antiarrhythmic		
ipratropium bromide	*[22254-24-6]*	$C_{20}H_{30}NO_3 \cdot Br$
Cholinergic		
acetylcholine bromide	*[66-23-9]*	$C_7H_{1}\ NO_2 \cdot Br$
benzylpyrinium bromide	*[587-46-2]*	$C_{15}H_{17}N_2O_2 \cdot Br$
demecarium bromide[a]	*[56-94-0]*	$C_{32}H_{52}N_4O_4 \cdot 2Br$
neostigmine bromide	*[114-80-7]*	$C_{12}H_{19}N_2O_2 \cdot Br$
pyridostigmine bromide[a]	*[101-26-8]*	$C_9H_{13}N_2O_2 \cdot Br$
Cholinesterase inhibitor		
distigmine bromide	*[15876-67-2]*	$C_{22}H_{32}N_4O_4 \cdot 2Br$
galanthamine hydrobromide	*[1953-04-4]*	$C_{17}H_{21}NO_3 \cdot HBr$
Counterirritant, topical		
3-bromo-*d*-camphor	*[76-29-9]*	$C_{10}H_{15}BrO$
Diagnostic aid (hepatic function)		
sulfobromophthalein sodium[a]	*[71-67-0]*	$C_{20}H_{10}Br_4O_{10}S_2 \cdot 2Na$
Diagnostic aid (radioactive imaging agent)		
mebrofenin in a ^{99m}Tc complex	*[78266-06-5]*	$C_{15}H_{19}BrN_2O_5$
Diagnostic aid (radiopaque medium)		
3′,3″,5′,5″-tetrabromophenolphthalein disodium salt	*[1301-21-9]*	$C_{20}H_{10}Br_4O_4 \cdot 2Na$
Heparin antagonist		
hexadimethrine bromide	*[9011-04-5]*	$(C_{10}H_{24}N_2 \cdot C_3H\ Br_2)_x$
Narcotic antagonist		
nalorphine hydrobromide	*[1041-90-3]*	$C_{19}H_{21}NO_3 \cdot HBr$
Neuromuscular blocker		
suxethonium bromide	*[111-00-2]*	$C_{1}\ H_{34}N_2O_4 \cdot 2Br$
Progestogen		
haloprogesterone	*[3538-57-6]*	$C_{21}H_{28}BrFO_2$
Radioprotective agent		
AET[b]	*[56-10-0]*	$C_3H_9N_3S \cdot 2BrH$
Sedative		
calcium bromolactobionate	*[33659-28-8]*	$C_{12}H_{22}O_{12} \cdot SBr_2Ca \cdot SCa$
Sedative and hypnotic		
acecarbromal	*[77-66-7]*	$C_9H_{15}BrN_2O_3$
d-bornyl α-bromoisovalerate	*[52964-40-6]*	$C_{15}H_{25}BrO_2$
brallobarbital	*[561-86-4]*	$C_{10}H_{11}BrN_2O_3$
bromoisovalum	*[496-67-3]*	$C\ H_{11}BrN_2O_2$
brotizolam	*[57801-81-7]*	$C_{15}H_{10}BrClN_4S$
butallylonal	*[1142-70-7]*	$C_{11}H_{15}BrN_2O_3$
carbromal	*[77-65-6]*	$C_7H_{13}BrN_2O_2$
diethylbromoacetamide	*[511-70-6]*	$C\ H_{12}BrNO$
haloxazolam	*[59128-97-1]*	$C_{17}H_{14}BrFN_2O_2$
ibrotamine	*[466-14-8]*	$C_7H_{14}BrNO$
propallylonal	*[545-93-7]*	$C_{10}H_{13}BrN_2O_3$
propiomazine	*[362-29-8]*	$C_{20}H_{24}N_2OS$
Sedative, hypnotic, and anticonvulsant		
narcobarbital	*[125-55-3]*	$C_{11}H_{15}BrN_2O_3$
Sedative, hypnotic, and antitussive		
bromoform	*[75-25-2]*	$CHBr_3$
Serotonin antagonist		
bromolysergide	*[478-84-2]*	$C_{20}H_{24}BrN_3O$
Skeletal muscle relaxant		
decamethonium bromide	*[541-22-0]*	$C_{1}\ H_{38}N_2 \cdot 2Br$
fazadinium bromide	*[49564-56-9]*	$C_{28}H_{24}N\ \cdot 2Br$
hexacarbacholine bromide	*[306-41-2]*	$C_{18}H_{40}N_4O_4 \cdot 2Br$
pancuronium bromide[a]	*[15500-66-0]*	$C_{35}H_{60}N_2O_4 \cdot 2Br$
pipecurium bromide	*[52212-02-9]*	$C_{35}H_{2}N_4O_4 \cdot 2Br$
succinylcholine bromide	*[55-94-7]*	$C_{14}H_{30}N_2O_4 \cdot 2Br$
vecuronium bromine	*[50700-72-6]*	$C_{34}H_{57}N_2O_4 \cdot Br$
Skeletal muscle relaxant and succinylcholine synergist		
hexafluorenium bromide	*[317-52-2]*	$C_{3}\ H_{42}N_2 \cdot 2Br$
Spasmolytic		

pinaverium bromide	*[53251-94-8]*	$C_{2}H_{41}BrNO_{4}\cdot Br$
Thiamine antagonist		
pyrithiamine	*[534-64-5]*	$C_{14}H_{19}N_{4}O\cdot BrH\cdot Br$
Thyroid inhibitor		
3,5-dibromo-L-tyrosine	*[300-38-9]*	$C_{9}H_{9}Br_{2}NO_{3}$
Uricosuric		
benzbromarone	*[3562-84-3]*	$C_{17}H_{12}Br_{2}O_{3}$
Used in treatment of diabetic neuropathy and retinopathy		
ponalrestat	*[72702-95-5]*	$C_{17}H_{12}BrFN_{2}O_{3}$
Used in the separation and determination of nucleic acids		
homidium bromide	*[1239-45-8]*	$C_{21}H_{20}N_{3}\cdot Br$
Used in the treatment of gastric disorders		
vitamin U bromide	*[33515-32-1]*	$C_{5}H_{14}NO_{2}S\cdot Br$
Vasodilator		
nicergoline	*[27848-84-6]*	$C_{24}H_{27}BrN_{3}O_{3}$
Vasodilator, peripheral		
brovincamine	*[57475-17-9]*	$C_{21}H_{25}BrN_{2}O_{3}$
Veterinary medicine		
bromofenofos	*[21466-07-9]*	$C_{12}H_{7}Br_{4}O_{5}P$
halofuginone	*[55837-20-2]*	$C_{16}H_{17}BrClN_{3}O_{3}$
homidium bromide	*[1239-45-8]*	$C_{21}H_{20}N_{3}\cdot Br$
resorantel	*[20788-07-2]*	$C_{13}H_{10}BrNO_{3}$

[a] Listed in the *U.S. Pharmacopeia* (197).

[b] Carbamimidothioic acid 2-aminoethyl ester dihydrobromide.

Miscellaneous Uses. Bromoform *[75-25-2]*, $CHBr_3$, is used in separating mixtures of minerals. *sym*-Tetrabromoethane *[79-27-6]*, $C_2H_2Br_4$, is used in microscopy, as a solvent, and separating minerals by density. 1-Bromonaphthalene *[90-11-9]*, $C_{10}H_7Br$, is used as an immersion fluid in determining the refractive index of crystals, for determining water in alcohol by the cloud point method, and for refractometric fat determination. Mixed with polymerized castor oil (qv) it is used as a general immersion oil in microscopy. *p*-Bromophenol *[106-41-2]*, C_6H_5BrO, is used as a disinfectant. Thonzonium bromide *[553-08-2]*, $C_{32}H_{55}N_4O$, is a detergent and tribromosalan *[87-10-5]*, $C_{13}H_8Br_3NO_2$, is a bacteriostat in detergents. Myristyltrimethylammonium bromide *[1119-97-7]*, $C_{17}H_{38}N\cdot Br$, is a disinfectant and deodorant. 1,2-Dibromo-2,4-dicyanobutane *[35691-65-7]*, $C_6H_6Br_2N_2$, is a preservative for latex paints (qv), adhesives (qv), latex emulsions, dispersed pigments (qv), joint cements (qv), and metal working fluids. Tribromoacetic acid *[75-96-7]*, $C_2HBr_3O_2$, is used as a polymerization catalyst. Tribromo-*tert*-butyl alcohol *[76-08-4]*, $C_4H_7Br_3O$, is a modifier in the polymerization of vinyl chloride. Bromoacetone *[598-31-2]*, C_3H_5BrO, α-bromobenzyl cyanide *[5798-79-8]*, C_8H_6BrN, *m*-xylyl bromide *[620-13-3]*, C_8H_9Br, *o*-xylyl bromide *[89-92-9]*, C_8H_9Br, and *p*-xylyl bromide *[104-81-4]*, C_8H_9Br, are used in war-gas formulations (see CHEMICALS IN WAR). 5-Bromouracil *[51-20-7]*, $C_4H_3BrN_2O_2$, is used experimentally as a mutagen.

Shipping and Precautions

Some bromine compounds are covered specifically under Hazardous Materials Regulations. Other compounds may usually be shipped under the classification of chemicals, not otherwise indexed by name, without special requirements unless from their nature they would fall under a category such as combustible liquid, compressed gas, corrosive liquid (or solid), disinfectant liquid (or solid), drug, dye intermediate (liquid), fire extinguisher, flammable gas (liquid or solid), insecticide, medicine, oxidizer or oxidizing material, poisonous liquid (gas or solid), solvent, or tear gas. Specific provisions apply to each of these categories and appropriate packaging and labeling are required.

In general, exposure to bromine compounds should be avoided. This applies to inhalation, ingestion, and skin contact, except under medical supervision. In case of skin contact, the affected parts should be washed thoroughly first with water, then with soap and water. Following any significant exposure medical treatment should be obtained promptly.

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BRONCHOLYTIC AGENTS.

See ANTIASTHMATIC AGENTS; EXPECTORANTS, ANTITUSSIVES, AND RELATED AGENTS; PROSTAGLANDINS.

BRONZE.

See COPPER ALLOYS.

BTX PROCESSING

Benzene *[71-43-2]* (B), toluene *[108-88-3]* (T), and the xylenes (X) are the lowest molecular weight aromatic hydrocarbon homologues. They are each very large scale chemical feedstocks. Since they are often produced together in the same process, they can be considered as a group, ie, BTX. However, BTX as such is not an article of commerce. It is either an important component of a crude mixture such as reformate or pyrolysis gasoline, or it is separated and purified into its individual components. This article mainly discusses the processes for making those crude mixtures. Other articles cover the physical and chemical properties of the individual BTX compounds themselves (see BENZENE; TOLUENE; and XYLENES AND ETHYLBENZENE). This article focuses on technology involving the group as a whole.

Originally BTX was obtained commercially by pyrolysis of coal (see COAL). Since World War II, the production of BTX has been intimately connected with the production of gasoline. BTX constitutes part of an important gasoline component called reformate which is discussed below (see GASOLINE AND OTHER MOTOR FUELS). Reformate is highly valued for gasoline because it has a very high octane rating. This results from the high concentration of aromatic compounds, all of which have very high octane values.

Any BTX needed for chemical use is separated from the reformate stream before it is blended into the gasoline pool. Although at a given refinery the total volume of gasoline production (eg, 16,000 m^3 d) usually dwarfs the BTX volume (eg, 800 m^3 d) and may have a higher priority, BTX production is often important enough to support its own reforming facilities and should not be considered simply as a gasoline by-product. This independence from gasoline may be even further emphasized in the future because of restrictions on the allowed level of BTX in gasoline and because new BTX processes may utilize light feeds or natural gas.

The need for BTX in gasoline has varied considerably. In the 1970s and 1980s in the United States, more high octane reformate was needed as the use of lead antiknock compounds was decreased for environmental reasons. More reforming capacity was put into use. Now there is environmental pressure to reduce the aromatic content (especially benzene) of gasoline (1). This may dramatically reduce production of gasoline reformate. Octane number requirements would have to be met with other high octane components such as oxygenated hydrocarbons (eg, methyl *t*-butyl ether (MTBE)). Therefore, the production of BTX for gasoline probably will drop. However, despite possible dislocations in supply, the demand for chemical uses will still be readily satisfied and the availability and price of BTX for chemical uses probably will not be greatly affected by the change in gasoline composition.

The principal chemical uses of BTX are illustrated in Figure 1 and listed in Table 1 (2). A very wide range of consumer products from solvents to fibers, films, and plastics are based on BTX. The consumption of BTX is approximately in the proportions of 67:5:28, respectively. However, no BTX process gives BTX in these proportions. The economic value of benzene and xylenes (especially *p*-xylene) is normally higher than that of toluene. Because of this, processes that convert toluene to benzene by hydrodealkylation (3) and disproportionate toluene to benzene and xylenes (4) have been commercialized. In addition, reforming processes that emphasize production of either benzene or *p*-xylene *[106-42-3]* have been described (5). Since these are not classified as BTX processes they are not discussed in detail here.

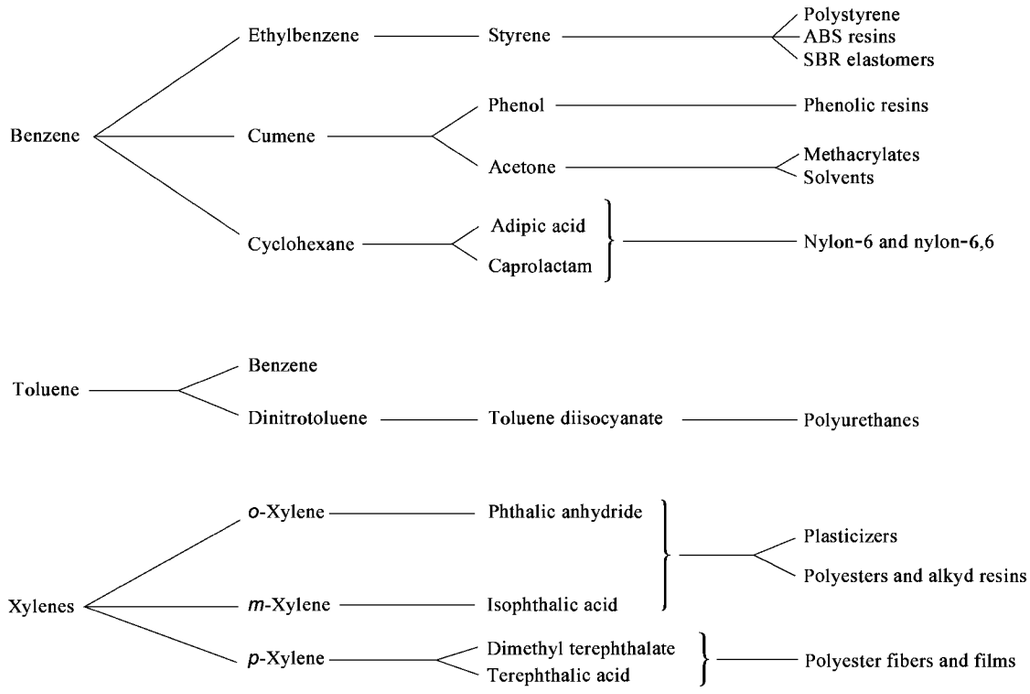

Fig. 1. Principal uses of BTX.

Table 1. Consumption of BTX in the Manufacture of Chemicals, 1989, 10^3 t

Product	Worldwide	United States
benzene		
cumene *[98-82-8]*	4,319	1,437
cyclohexane *[110-82-7]*	3,656	915
ethylbenzene *[100-41-4]*	10,863	3,248
all others	3,157	568
Total (benzene)	*21,995*	*6,168*
toluene		
cresol *[1319-77-3]*	93	
phenol *[108-95-2]*	271	36
toluene diisocyanate *[1321-38-6]* and toluenediamine *[26764-44-3]*	602	241
all others	564	194
Total (toluene)	*1,530*	*471*
o-xylene		
phthalic anhydride *[85-44-9]*	1,964	393
p-xylene		
dimethyl terephthalate *[120-61-6]*	2,349	870
terephthalic acid *[100-21-0]*	4,990	1,363
Total (o- and p-xylene)	*9,303*	*2,626*

Reforming

Reforming, as currently practiced, is a platinum-catalyzed high temperature vapor-phase process which converts a relatively nonaromatic C –C_{12} hydrocarbon mixture (naphtha) to an aromatic product called reformate (6). The catalyst often contains less than 1% of platinum, possibly modified with other metals, supported on a high surface area support such as alumina, which provides acidity (see CATALYSIS). The gasoline octane rating of the reformate is directly related to its aromatic content (Fig. 2). The aromatic content is higher when the reformer is operated at high severity (high temperature, low space velocity). Some cracking to light products also occurs, and this also increases at high severity. A typical reformate contains BTX in the proportions of 19 49 32, respectively, although these proportions can be varied by tailoring the feed composition. In response to the environmental pressure on benzene in motor gasoline mentioned previously, it is probable that many U.S. refiners will choose to reduce the proportion of benzene in their reformate by raising the cut point on the naphtha feed to their reformers.

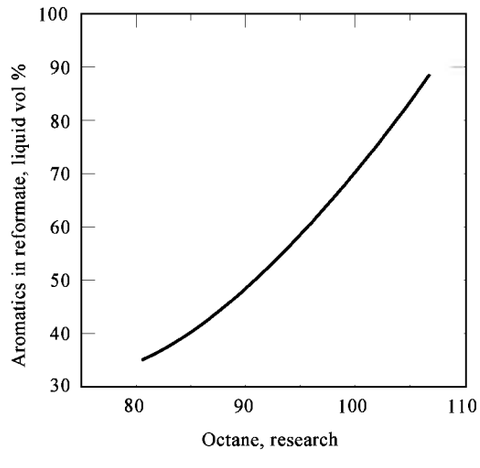

Fig. 2. Octane rating as a function of aromatics in reformate.

Feedstock. Feed for reformers is normally petroleum hydrocarbons that boil roughly in the 70–190°C range. When this feed (straight run naphtha) is obtained by fractionating a crude oil, its composition varies considerably with the source of the crude as shown in Table 2 (see PETROLEUM) (7). The aromatic content of these naphthas is quite low. Because of this and the lack of highly branched paraffins, the octane numbers are low. Also, some naphthas have high cycloparaffin (naphthene) contents. Since, in the reforming process, open chain paraffins first have to cyclize to cycloparaffins before they aromatize, those naphthas with high cycloparaffin content are generally easier to reform.

Table 2. Properties of Straight Run Naphthas from Various Crude Oils

Crude properties			Naphtha properties					
Name (source)	Gravity, °API	Sulfur, wt %	Vol % of crude	Gravity, °API	Octane, research	Paraffins, wt %	Cyclo-paraffins, wt %	Aromatics, wt %
Arab Light (Saudi Arabia)	33.1	1.9	17.0	59.2	33.2	72	17	11
Arab Heavy (Saudi Arabia)	27.4	2.8	13.0	59.9	33.9	70	19	11
Iran Light (Iran)	33.5	1.4	17.8	56.2	45.9	59	28	13
Bonny Light (Nigeria)	34.3	0.1	16.1	51.9	63.0	37	51	12
Sumatra Light (Indonesia)	35.9	0.1	10.9	58.0	41.8	58	37	5
Ardjuna (Indonesia)	36.0	0.1	21.7	50.9	66.5	36	45	19
Brent (North Sea, UK)	38.2	0.4	20.2	54.0	62.3	47	39	14
Mayan (Mexico)	21.5	3.4	12.0	56.9	45.3	62	26	12
Isthmus (Mexico)	33.3	1.2	19.2	56.5	65.9	61	26	13

Alaska North Slope (Alaska, U.S.)	27.6	1.1	13.3	52.1	63.2	42	41	17
Huntington Beach (California, U.S.)	21.8	1.5	14.1	48.2	70.6	14	80	6
West Texas Intermediate (Texas, U.S.)	39.1	0.3	23.4	54.6	53.8	45	45	10
Empire Mix (Gulf Coast, U.S.)	32.3	0.3	12.7	52.4	61.2	43	44	13

In addition to straight run naphthas, 70–190°C cuts obtained by distillation from streams produced by cracking high boiling petroleum fractions can also be used as feed to reformers. Naphthas produced by hydrocracking are particularly suitable.

Impurities containing sulfur, nitrogen, and oxygen are undesirable in a reformer feed because they harm the catalyst. Therefore, these elements are largely removed by pretreating the feed with hydrogen (hydrotreating) in the presence of catalysts containing nickel–molybdenum, cobalt–molybdenum, or combinations (6). This process converts them into hydrogen sulfide, ammonia, and water, respectively, which are readily removed by distillation.

The molecular weight distribution of the feed affects the distribution of the product. If the naphtha is concentrated in the C –C_8 range, more benzene and toluene are found in the product. If the feed is weighted to C_8–C_{10}, more xylenes and higher aromatics are found. Some carbon number "slippage" occurs by dealkylation: some C_7s form benzene by losing a methyl group, some C_8s form toluene, etc.

Reforming Conditions. The main process variables are pressure, 450–3550 kPa (50–500 psig), temperature (470–530°C), space velocity, and the catalyst employed. An excess of hydrogen (2–8 moles per mole of feed) is usually employed. Depending on feed and processing conditions, net hydrogen production is usually in the range of 140–210 m^3 m^3 feed (800–1200 SCF bbl). The C_1–C_4 products are recovered and normally used as fuels.

A flow diagram for a typical semiregenerative reformer based on the Rheniforming Process (8) is shown in Figure 3. The hydrotreated feed is heat exchanged with the reformer product. Further heating is achieved by passage through a furnace. The feed then enters the first of several reactors which, in the Rheniforming Process, contain platinum–rhenium on alumina catalyst. To replenish the endothermic heat of reaction of the aromatization process, several sets (three are shown in Fig. 3) of alternating furnaces and reactors are used.

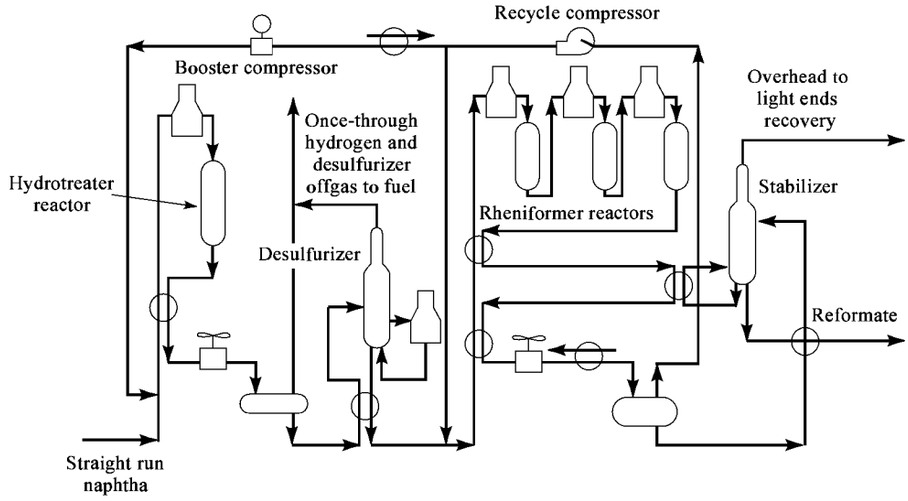

Fig. 3. Simplified process flow diagram of a naphtha hydrotreater and rheniformer.

The excess hydrogen present actually inhibits aromatics formation but is necessary to reduce catalyst fouling by coke formation. Catalyst fouling is a critical issue in reforming. Process conditions and catalyst compositions balance conversion against fouling rate. Today, by using improved catalysts that foul more slowly or by using continuous catalyst regeneration, commercial reformers can get high conversions and yields by operating at relatively low pressures, eg, 450–965 kPa (50–125 psig). Figure 4 shows the effects of pressure (mainly partial pressure of hydrogen) and of conversion on BTX yield.

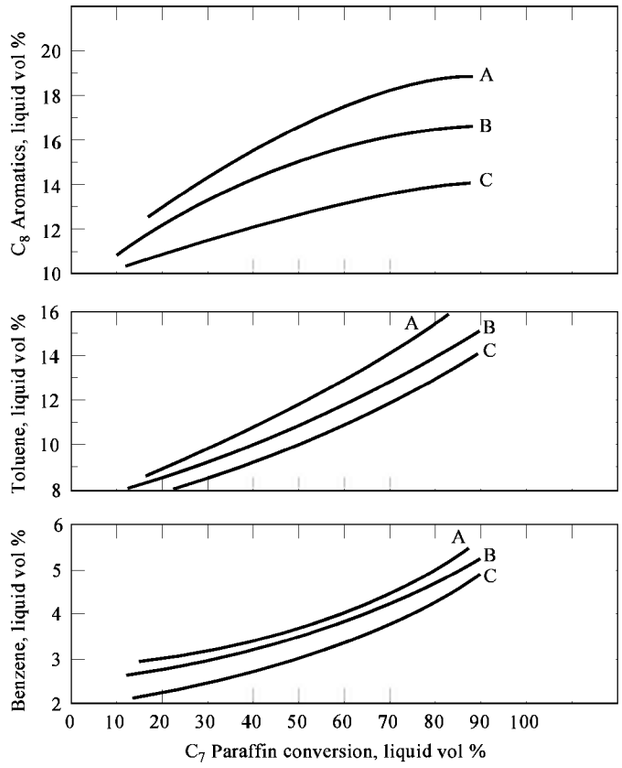

Fig. 4. Higher yields from lower pressures; reactor pressure: A, 791 kPa (100 psig); B, 1480 kPa (200 psig); C, 2515 kPa (350 psig). Data for Arabian Naphtha, 54–154°C fraction.

As coke fouling occurs, the catalyst loses activity. Temperature must be raised to keep the conversion level constant. Typically only about a 20–30°C temperature rise is allowable. Then the very valuable platinum catalyst must be regenerated. Three approaches are used. If the run length (fouling time) is about six months or more, it is practical to shut down the unit and regenerate the catalyst in place. This approach, called semiregenerative reforming, is used in a number of commercial processes: Houdriforming, Magnaforming, Platforming, and Rheniforming (6).

If, because of feed type, process severity, or catalyst composition, the run length is short, the catalyst is regenerated in swing reactors or continuously. Processes using four to six reactors, one or more of which may be undergoing regeneration at any given time, have been developed, eg, Powerforming and Ultraforming (6). The catalyst has a higher average activity in these processes than in semiregenerative ones. Continuous regeneration is offered by UOP in the Continuous Catalyst Regeneration (CCR) Platforming Process, and by IFP in their Aromizing Process (9). A portion of the catalyst is continuously removed, regenerated in a separate regeneration loop, and returned to the reformer (see CATALYSTS, REGENERATION).

During regeneration the coke is burned off the catalyst. The techniques employed are fairly sophisticated so as to maintain the platinum and any other active metals in a well dispersed form and to restore the original catalyst activity. Regeneration usually takes several days.

The choice of reforming process depends on the product desired, plant size, and capital availability. If BTX is to be only a coproduct, the refiner might select a semiregenerative process. Severity is usually lower, and the important factor is the yield of gasoline. This yield for some combinations of feeds and catalysts can improve with successive catalyst regeneration cycles (10). For high BTX yields a swing reactor or continuous regeneration process might be the choice because BTX yields are highest at high severity and low pressure.

Patents cover a new reforming catalyst based on L-zeolite which gives a significantly higher yield of BTX, especially benzene, from light paraffinic feeds (11). Other new zeolites (12) may also offer advantages over the traditional reforming catalyst supports.

Reforming Chemistry. The main reactions occurring in a reformer are shown in Figure 5 (6,13–15); most are reversible indicating the potential importance of reaction equilibrium.

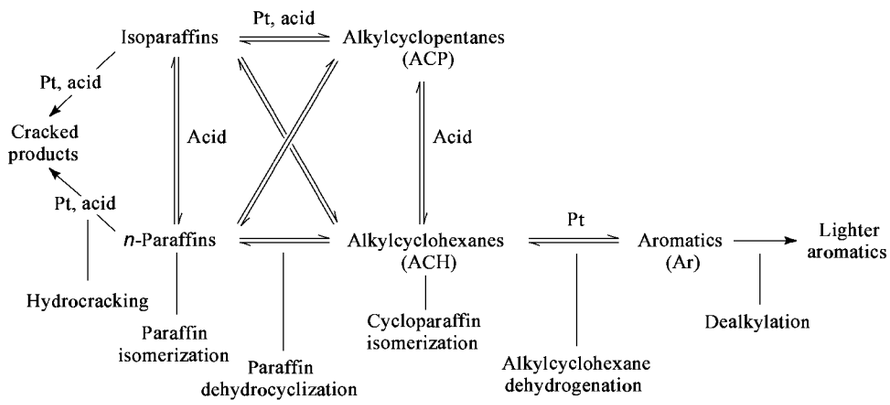

Fig. 5. Main reactions of catalytic reforming. Pt and acid refer to predominant active catalytic sites.

In the alkylcyclohexane (ACH) to aromatic equilibrium, ACH $\rightleftharpoons$ Ar, aromatics are favored by high temperatures and low pressures. Normal reforming conditions promote rapid ACH dehydrogenation and a high conversion to aromatics.

The alkylcyclopentane (ACP) to aromatics process (ACP $\rightleftharpoons$ ACH $\rightleftharpoons$ Ar) is less efficient than ACH dehydrogenation, owing to the slowness of the first step and to ACP ring opening. Under conditions where cyclohexane is converted to benzene with close to 100% efficiency, only 50–75% of methylcyclopentane may be converted to benzene.

Aromatization of isoparaffins and *n*-paraffins is more difficult. Not only is the reaction slower, but also the ultimate yield is lower because more

cracking occurs. Under mild reforming conditions a straight run naphtha with a high cycloparaffin (naphthene) plus aromatic content achieves a much higher octane rating (and aromatics content) than one with a high paraffin content. This latter naphtha can be more severely reformed to achieve a high octane rating, but then the yield of liquid product is lower.

Hydrocarbon Pyrolysis

A large amount of BTX is obtained as a by-product of ethylene manufacture (see ETHYLENE). The amount produced strongly depends on the feed to the ethylene plant. This is illustrated in Table 3 for various feeds to a typical large scale plant producing 450,000 t yr of ethylene (16). Note that only about 1–2% of the ethane propane feeds end up as BTX and it is almost completely benzene and toluene. As the feed goes up in molecular weight, the yield of BTX increases from 4% with butane feed to about 10% with gas oils, and the BTX proportions go from 72:20:8 respectively, to 44:34:22 respectively.

Table 3. BTX Yields from Various Pyrolysis Feeds,[a,b] 10^3 t/yr[c]

Feed	C_2H	C_3H_8	n-C_4H_{10}	Mid-crude naphtha	C –C_8 Raffinate	Gas oil, distilled	
						Atm	Vac
ethylene product rate	450	450	450	450	450	450	450
feed rate	583	1080	1135	1349	1535	1750	2213
ethylene[d]	48.2	34.2	35.8	30.0	26.0	23.0	18.0
benzene	5.0	26.6	34.3	90.0	72.7	105.5	82.5
toluene	0.7	5.8	9.4	45.1	41.5	50.8	64.3
C_8 aromatics			4.0	23.8	18.4	38.0	41.4

[a] Ethane recycled to extinction.

[b] Ref. 16.

[c] Unless otherwise noted.

[d] Once through yield.

Outside the realm of typical hydrocarbon pyrolysis is the high temperature pyrolysis of methane. In one variant of this process, which has only been commercialized to produce acetylene (with some BTX), methane reacts in an electric arc at about 1500°C (17) with very short contact times. At higher temperatures or with a catalyst and added hydrogen, BTX is produced with fairly high selectivity (18).

BTX from Light Hydrocarbons

A completely new approach for BTX production has emerged in recent years. It converts C_2 to C paraffins into aromatics using a modified ZSM-5 zeolite catalyst which contains gallium (19). An example of this approach, the Cyclar process, has been in commercial operation by British Petroleum at Grangemouth, Scotland since August 1990 (20). It uses C_3–C_4 feed and employs UOP's CCR technology to compensate for rapid catalyst coking.

The mechanistic steps are as follows: paraffins dehydrogenate to olefins; the olefins oligomerize and cyclize; and the cyclics aromatize. Because the first step is rate controlling, very little olefin is actually present. The BTX product is relatively free of nonaromatics and therefore is very desirable as a chemical feed. As in reforming, some C_1–C_2 fuel gas is produced along with a valuable hydrogen stream. From a C_3–C_4 feed the BTX product is roughly 35:45:20, respectively.

Other BTX Processes

Because of the importance of the petroleum-based processes discussed previously, only about 1% of the U.S. supply of BTX currently comes from coal pyrolysis (21).

Outside the United States, coal pyrolysis is more important as a source of BTX. The proportions are about 70:20:10, but can vary greatly depending on the coal and on the pyrolysis process used. Product quality is not as good as petroleum-derived BTX. This source could become more important again if petroleum costs escalate. Much higher yields of BTX from coal can be obtained by first hydrogenating the coal (22).

Another very interesting route to BTX is the Mobil Methanol To Gasoline (MTG) Process (23). Methanol is converted into gasoline containing about 50% aromatics by passing it over a ZSM-5 catalyst. The BTX composition is about 10:20:70, respectively. More than half of the aromatics present are C_9s and C_{10}s, and these would have to be dealkylated to yield more BTX. The methanol can be obtained from any syngas source such as coal, natural gas, or petroleum (see METHANOL). The economic attractiveness of this approach depends on the cost of methanol relative to gasoline from petroleum. A commercial plant has been operating successfully since 1985 in New Zealand where natural gas is abundant and petroleum is scarce (24).

BTX Recovery

The complexity of separating and purifying the individual BTX components from crude BTX products depends on the amount of nonaromatic impurities present. If the amount is small enough, simple distillation can suffice. If not, it is obvious from Figure 6 that distillation alone will not be sufficient because the BTX aromatic compounds are close in boiling point to some of the cycloparaffins of the same carbon number or to paraffins of the next higher carbon number. Because of this, extraction or extractive distillation with a polar solvent is used to separate the slightly polar aromatic hydrocarbons from the nonpolar nonaromatic hydrocarbons. When olefins are also present, as in pyrolysis gasoline, these interfere with the extraction and must first be hydrogenated or removed by adsorbents.

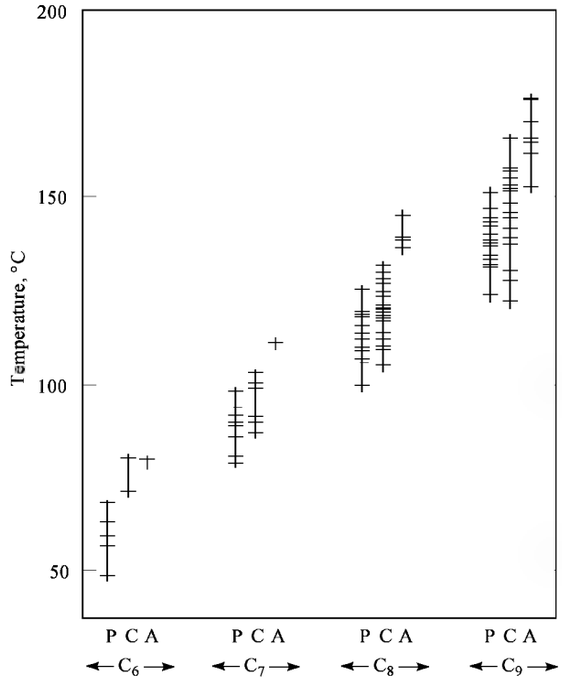

Fig. 6. Boiling points of C –C_9 hydrocarbons. P, iso and normal paraffins; C, C_5- and C -cycloparaffins; and A, aromatics.

An option for avoiding the cost of extraction is to increase the severity of the BTX formation step. This reduces the quantity of residual paraffins, and, depending on the BTX formation process, may leave the BTX clean enough to purify by distillation. The final impurity concentrations may still be too high for merchant sale, but may be acceptable in some downstream operations. For example, xylenes going into an isomerization separation loop for *p*-xylene production can contain some paraffins if the isomerization catalyst is capable of decomposing them. Disadvantages of high severity processing are the increased catalyst fouling rate and the potential increase in undesirable olefin impurities.

Extraction and Extractive Distillation. The choice of an extraction or extractive distillation solvent depends upon its boiling point, polarity, thermal stability, selectivity, aromatics capacity, and upon the feed aromatic content (see EXTRACTION). Capacity, defined as the quantity of material that is extracted from the feed by a given quantity of solvent, must be balanced against selectivity, defined as the degree to which the solvent extracts the aromatics in the feed in preference to paraffins and other materials. Most high capacity solvents have low selectivity. The ultimate choice of solvent is determined by economics. The most important extraction processes use either sulfolane or glycols as the polar extraction solvent.

Sulfolane *[126-33-0]*, used in UOP and Shell processes (25,26), offers good thermal and hydrolytic stability, high density and boiling point, and a good balance of solvent properties. Its high density and boiling point make it easy to separate from the hydrocarbon streams. A diagram of a sulfolane extraction unit is shown in Figure 7. Fresh feed enters the extractor and flows countercurrent to the down flowing solvent. The raffinate is withdrawn at the top of the extractor and leaves the system after water washing. The solvent, now rich in aromatics, is sent to the top of the extractive stripper where the nonaromatic hydrocarbons are removed. Aromatics and sulfolane are separated in the recovery column. The lean solvent is recycled to the extractor and the aromatics are washed with water and removed. The recovery of benzene and toluene is usually 99+%; of C_8 aromatics 97% and of C_9^+ aromatics 75–90%.

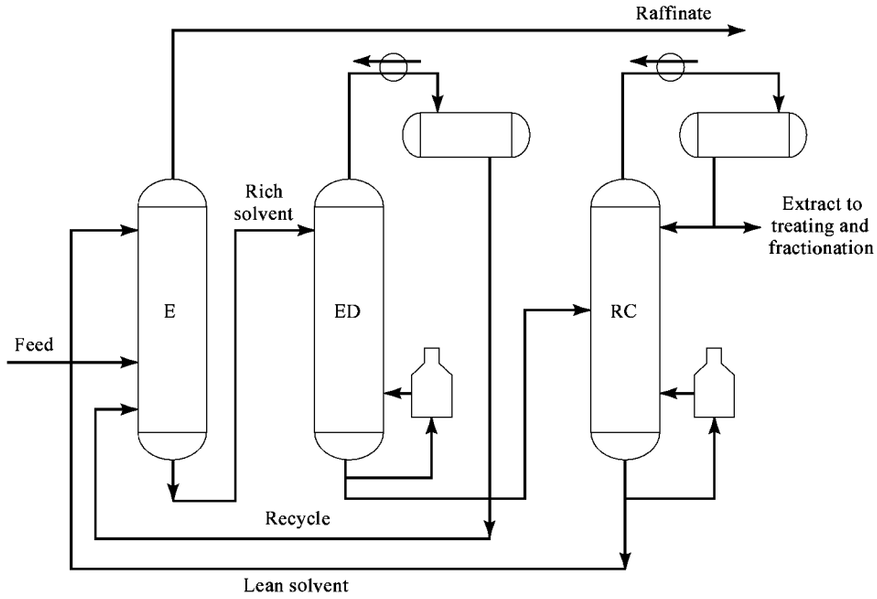

Fig. 7. Shell sulfolane extraction process. E, extraction; ED, extractive distillation; RC, recovery column.

Courtesy of UOP, Inc.

The widely employed UOP Udex Process uses a glycol solvent (27). Diethylene glycol was used in early versions of the process; however, increased capacity was obtained by adding dipropylene glycol or, in some cases, a change was made to triethylene glycol. Further improvement was made by using tetraethylene glycol (28). The Union Carbide Tetra Process also employs tetraethylene glycol (29). Other extraction processes are included in Table 4.

Table 4. Extractive Processes for BTX Recovery

Company process	Solvent	CAS Registry Number	Reference
Extraction			
Shell Process	sulfolane	[126-33-0]	25,26
UOP Udex Process	diethylene glycol	[111-46-6]	27
	triethylene glycol	[112-27-6]	
	tetraethylene glycol	[112-60-7]	28
Union Carbide Tetra Process	tetraethylene glycol	[112-60-7]	29
Lurgi Arosolvan		[872-50-4]	30,31
	N-methyl-2-pyrrolidinone and monoethylene glycol	[107-21-1]	
Institut Fran3ais du Petr¢le	dimethyl sulfoxide (DMSO)	[67-68-5]	32
SNAM Progetti Formex	*N*-formylomorpholine	[4394-85-8]	33
Howe-Baker Aromex	diglycolamine	[929-06-6]	34
Krupp-Koppers Morphylex	*N*-formylmorpholine	[4394-85-8]	35
Extractive distillation			
Institut Fran3ais du Petr¢le DMF	dimethylformamide (DMF)	[68-12-2]	5
Krupp-Koppers Octenar	*N*-formylmorpholine	[4394-85-8]	5
Lurgi Distapex	*N*-methyl-2-pyrrolidinone	[872-50-4]	5
UOP Sulfolane	sulfolane	[126-33-0]	5

Extractive distillation, using similar solvents to those used in extraction, may be employed to recover aromatics from reformates which have been prefractionated to a narrow boiling range. Extractive distillation is also used to recover a mixed benzene–toluene stream from which high quality benzene can be produced by postfractionation; in this case, the toluene product is less pure, but is still acceptable as a feedstock for dealkylation or gasoline blending. Extractive distillation processes for aromatics recovery include those listed in Table 4.

Downstream Processing. In addition to extraction, various downstream operations are often carried out on the BTX product to produce products in proportions to fit the market demand. A typical aromatics processing scheme is shown in Figure 8 in which benzene, *p*-xylene, and *o*-xylene are the products.

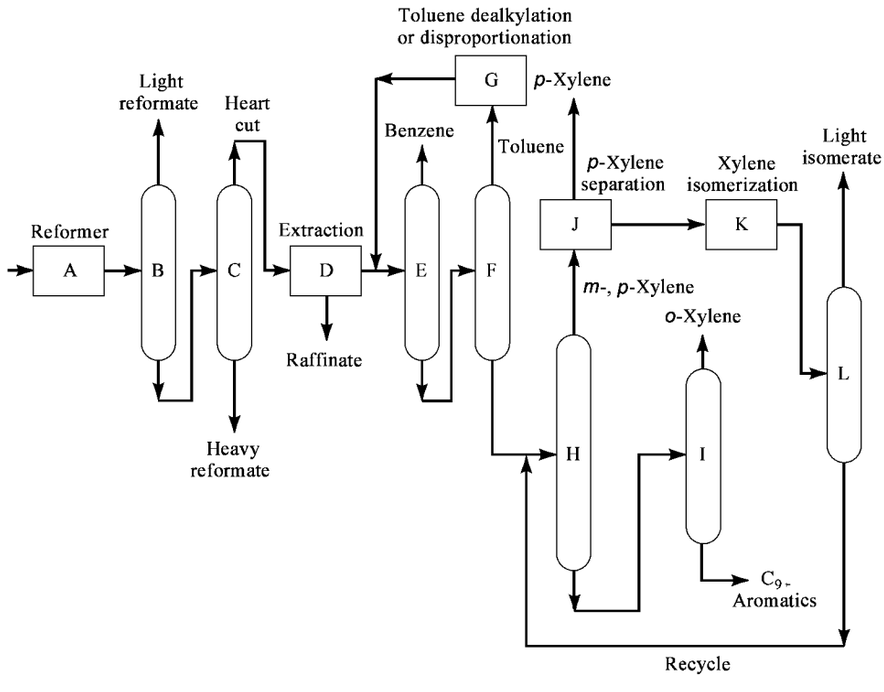

Fig. 8. General BTX processing sequence.

After the crude BTX is formed, by reforming in this case, a heart cut is sent to extraction. Actually, the xylenes and heavier components are often sent to downstream processes without extraction. The toluene produced is converted to benzene, a more valuable petrochemical, by running it through a hydrodealkylation unit. This catalytic unit operates at 540–810°C with an excess of hydrogen. Another option is to disproportionate toluene or toluene plus C_9 aromatics to a mixture of benzene and xylenes using a process such as UOP's Tatoray or Mobil's Selective Toluene Disproportionation Process (STDP) (36).

The *o*-xylene [95-47-6] in Figure 8 is recovered by a two-stage distillation. First it is separated (or split) from *m*-xylene [108-38-3] and the other C_8 aromatics in a superfractionating column, the xylene splitter, (Unit H). The bottoms, a mixture of *o*-xylene and C_9^+ aromatics, is redistilled (or rerun) in Unit I to recover *o*-xylene of 96+% purity.

The distillate (overhead) from Unit H, containing mostly ethylbenzene [100-41-4], *p*-xylene, and *m*-xylene, and some *o*-xylene becomes the feed for the *p*-xylene separation process (Unit J).

p-Xylene [106-42-3] can be purified by crystallization or adsorption. When a typical reformate-derived C_8 aromatic mixture is cooled, *p*-xylene crystallizes first. Most plants employing crystallization operate at 60 to 75°C, depending on feed composition (37). The process is limited by a eutectic temperature below which *o*- or *m*-xylene also crystallize. The solubility of *p*-xylene in the remaining C_8 aromatic mixture over the range of 60 to 75°C is 9.6 to 6.2%.

UOP's Parex Process can be used to purify *p*-xylene by adsorption (38). Toray has a similar process. These processes take advantage of the fact that *p*-xylene is adsorbed more easily than the other C_8 aromatics by a suitable molecular sieve. The *p*-xylene is desorbed by either a lighter or heavier hydrocarbon which is subsequently removed by distillation. *p*-Xylene is recovered in about 97% yield (see ADSORPTION).

The mother liquor obtained from the crystallization, or the raffinate after removal by adsorption, is isomerized using an acidic catalyst to convert *m*-xylene to the *o*- and *p*-isomers (Unit K in Fig. 8).

In the isomerization step, light and heavy impurities are generated, including saturated hydrocarbons, benzene, toluene, and C_9^+ aromatics. These are removed by recycling the isomerate through the xylene splitter and the light isomerate column (Unit L). If the light isomerate contains much benzene or toluene, it can be recycled to Unit G. *m*-Xylene may be recovered between the xylene splitter and the *p*-xylene separation plant by selective sulfonation followed by regeneration or via complex formation with a mixture of HF and BF_3 (39).

To this point the presence of ethylbenzene in the mixed xylenes has been ignored. The amount can vary widely, but normally about 15% is present. The isomerization process must remove the ethylbenzene in some way to ensure that it does not build up in the isomerization loop of Figure 8. The ethylbenzene may be selectively cracked (40) or isomerized to xylenes (41) using a platinum catalyst. In rare cases the ethylbenzene is recovered in high purity by superfractionation.

There are many variations of the basic processing loop shown in Figure 8. Processing to produce only BT is common, often in conjunction with a toluene-to-benzene dealkylation unit. If benzene and toluene are not to be recovered, Column B may be used to remove toluene and lighter components. In that case, Units E, F, and G would be eliminated. To recover *p*-xylene only, the xylene splitter is reduced in size and is used to split between *o*-xylene and the C_9^+ aromatics. The *o*-xylene rerun still is then eliminated.

Environmental Considerations

BTX processing has come under steadily increasing pressure to reduce emissions and workplace exposures (see INDUSTRIAL HYGIENE). Reductions in the permissible levels of both benzene and total aromatics (BTX) in gasoline have been legislated. Whereas all BTX components are to be controlled, the main focus is on benzene because it is considerably more toxic than the others and is classified as a known carcinogen (42).

Workplace exposure limits for benzene have been regulated to levels as low as 0.5 ppm (43). Industrial emissions affecting the public are now low enough that the EPA considers that a greater hazard exists from mostly indoor sources such as smoking, automobile exhausts, and consumer products (44).

The stringent controls over manufacturing and handling benzene may dissuade refiners from installing new equipment to extract benzene from gasoline to satisfy gasoline requirements. Instead they will probably modify their reforming operations to produce less benzene or to convert the remaining benzene to other compounds. They will achieve the necessary octane rating for gasoline via branched paraffins and oxygenates. Overall, this is likely to result in further segregation of petrochemicals BTX production from gasoline production.

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BUBBLE MEMORY.

See MAGNETIC MATERIALS, BULK; MAGNETIC MATERIALS, THIN FILMS AND PARTICLES.

BUILDING MATERIALS

Survey,
Plastic,

SURVEY

This article discusses traditional building and construction products, ie, not made from synthetic polymers (see BUILDING MATERIALS, PLASTIC), including wood, asphalt, gypsum, glass products, Portland cement, and bricks. The article presents information about each basic material, the products made from it, the basic processes by which the products or materials are produced, estimates of the quantity or dollar value of the quantities produced or used in the United States, and some pertinent chemical or physical properties related to the material. More detailed chemical and physical property data can be found in articles devoted to the individual materials (see ASPHALT; CEMENT; GLASS; WOOD).

Wood

Wood (qv) is arguably the oldest building material used by humans to construct their dwellings. It is a natural product obtained from trees, used in both structural and decorative applications. The chemical composition of wood is largely cellulose (qv) and lignin (qv). Today there are a variety of composite or reconstituted wood products, such as plywood, particle board, wood fiber boards, and laminated structural beams, where small pieces of wood or wood fiber are combined with adhesives to make larger sheets or boards (see LAMINATES).

Woods are classified as either hardwoods or softwoods, based on the seed- and leaf-type of the trees from which the wood comes. Softwoods come from trees that are classified as gymnosperms, or naked seeds, whereas the hardwoods are angiosperms, or covered seeds. The common softwoods, such as pine, spruce, fir, cedar, and hemlock, have specific gravities between 0.30 and 0.55, which make them ideal for construction purposes. They can be worked, ie, cut and shaped easily, with simple tools and can be nailed without splitting. Common hardwoods, such as oak, maple, and fruit woods, have higher specific gravities. They are harder to cut with hand tools and tend to split when nailed. Lower specific gravity hardwoods, such as balsa, are too weak for structural application. Because of these properties, softwoods are the common construction wood rather than the generally stronger hardwoods.

Manufacture. The manufacture of lumber or sawn wood starts with cutting the tree and removing the limbs (limbing), followed by sawing the log into slabs parallel to the long direction of the log. Most softwoods are cut either by sawing through and through or around the log (Fig. 1). Through and through sawing is done by cutting slabs of the desired thickness one after the other across the diameter of the log. Sawing around the log is done by cutting slabs of the desired thickness about one-third the way across the diameter of the log, rotating the log 90°, cutting more slabs, and then repeating the process. This leaves a solid center section that also can be cut. Quality hardwood is cut through and through or by sawing around, but it is also quartersawn. Quartersawn wood is considered to be more dimensionally stable. First the log is cut into quarters, then each quarter is sawn at a 45° angle to the flat sides (Fig. 1). The slabs can then be cut to width prior to or after drying.

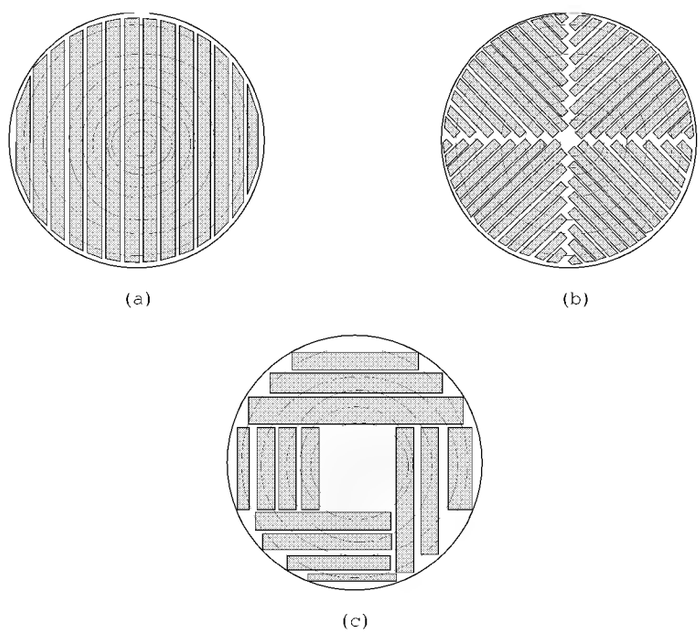

Fig. 1. Methods of sawing logs into slabs, where (**a**) is through and through, (**b**) is quartersawn, and (**c**) is sawing around.

The green wood of a fresh cut tree can have a moisture content of 60 to over 150% , depending on species and weather conditions. Hardwoods tend to have lower moisture contents than softwoods. These moisture levels are too high for most construction applications as the wood can rot and undergo relatively large dimensional and shape changes as it dries out. Most construction wood is dried to below 19% moisture content, often to about 8% , to reduce these problems. As wood drys, it typically shrinks 5–8% perpendicular to, ie, across, the grain and less than 1% with, ie, parallel to, the grain.

Construction lumber is milled, ie, smoothed, after it has dried to its finished dimensions. These dimensions are less than the nominal size of the lumber which is based on the size of the green wood cut during the sawing operation. Nominal versus actual sizes of construction lumber in the United States is given in Table 1.

Table 1. Softwood Nominal vs Actual Sizes, in.[a]

Nominal	Actual
1	s
2	1S
3	2S
4	3S

6	5S
8	7j
10	9j
12	11j

[a] To convert inches to cm, multiply by 2.54.

Finished lumber is visually sorted or graded based on industry organization standards. These standards consider the number of knots, ie, tree limb locations, straightness, and overall quality of the wood. For example, pine lumber graded #3 is full of knots whereas select-grade has almost no knots. Construction lumber is graded and stamped on the end of the boards. General grading classifications are given in Table 2, which shows that these gradings are qualitative and subjective.

Table 2. Softwood Gradings[a] by Wood Type

Grade classification			
Douglas fir	Redwood	Pine	Uses
C and better	clear all heart	C and better, 1 and 2 clear	exposed wood and where best weather resistance needed
C select	heart C	select, choice	contains slight defects; use for painted surfaces
construction	construction, construction heart	D select	some knots, some warping and cupping; use for finish construction
standard	merchantable	1–5 common	visible surface irregularities; use for framing

[a] As the use description shows, the quality of the wood decreases reading down each column.

Shake Shingle. Whole wood products are used in shake shingles for residential and light commercial application. Cedar is the most common wood used because it splits easily and is rot-resistant, but pine is also used. The logs are cut into approximately 12 in. (30.5 cm) lengths, split by hand or machine into slabs parallel to the grain, and classified as lightweight, medium weight, or heavyweight shingle based on thickness. The shingles are then nailed over a waterproofing felt, typically a nonperforated asphalt saturated organic felt, to provide water tightness to the roofing system. To obtain a class C fire rating, which is the lowest possible, from Underwriters Laboratory, a fire-retardant treatment is given to the wood shingles.

Annual Production. The United States is the largest single producer of lumber with about 25% of all the logs cut in the world. The current soft housing and construction markets as well as environmental pressures to limit logging are reducing the percentage. Still the value of wood harvested was about $12.6 billion in 1989.

The value of lumber produced in 1989 was estimated to be $17.3 billion, of which softwood lumber represented about 58%. The other 42% was composed of hardwood lumber (12%), woodchips (10%), and a variety of wood products (20%).

WOOD PRODUCTS OR COMPOSITE WOOD MATERIALS

The wood products or composite wood materials consist of products where the wood is cut into small and or thin pieces and then the cut pieces are glued together to form a larger piece of wood product. The most common example is plywood. This category also includes reconstituted wood products subclassified into wood flake boards, particle boards, or wood fiberboards depending on the size of the wood particle glued together. Products in these categories include low density fiberboard (wood fiberboard), medium density fiberboard (MDF), high density fiberboard (hardboard), flake board, oriented strand board (OSB), and particle boards.

Plywood. Plywood is made up of thin layers (plies) of wood laminated together. The plies alternate the grain direction to balance both the structural strength and the dimensional movement of wood. An odd number of plies is used to give an even number of adhesive lines and hence reduce warpage. The adhesive lines shrink during the curing process and cause warping; by having an even number of adhesive lines uniformly spaced throughout the cross section of the plywood panel, the shrinkage forces balance out. Plywood is considered to be more dimensionally stable than wood itself because of the dimensional stability of the cured resin adhesive and the cross-directional plies that balance and or cancel out most of the wood movement. Plywood is also favored for its resistance to splitting and punctures in normal construction applications. Thicknesses range from j (0.63 cm) to s in. (1.9 cm) with the common sheet dimension of 4 × 8 ft (1.2 × 2.4 m). The number of plies commonly range from three to five, but hardwood plywoods may have more. The outermost plies are called faces or face plies. Inner plies with the grain parallel to the face are called core(s) or center, whereas those with the grain direction perpendicular to the face are called the crossbands.

Some of the newer structural plywoods are called four-ply plywood, implying that they have an even number of plies. To get stability, two center crossbands are glued with the grains of the plies parallel, making it effectively one ply with the adhesive line in the neutral axis, and removing the warping tendency. These products can be considered a three-ply plywood. In general, the more plies the stronger the plywood is at a given thickness.

Plywood is also divided into softwood and hardwood plywood products. The classification depends on the type of wood the face plies are made from. The principal application for 1 cm and thicker hardwood plywoods are cabinets and furniture. The thinner grades are used to make paneling and doorskins, which represent approximately 56% of the total hardwood plywood products. The total market in 1989 was estimated to be $2.1 billion.

Softwood plywood is usually used for construction application and is the type commonly found in local lumber and home center stores. The face plies are generally fir. Shipments in 1989 were estimated at $5.02 billion. The Pacific Northwest represented 42% of the total whereas 36% came from the South.

Hardwood and softwood plywoods are manufactured by the same basic process. The first step is to make the veneers that are used as the plies. They are produced by slicing off thin layers of wood from presoftened logs that have been debarked and soaked in hot water for a period of time. The most common method of slicing the veneer is the rotary process, which uses a lathe to turn the log while a long sharp knife blade is pressed against the log. The knife is indexed to keep cutting at the desired thickness of veneer as the diameter of the log is reduced. Veneer comes off the log in a continuous sheet that is then cut into usable sizes and dried. Some hardwood plywood veneer is made by flat slicing. Flat slicing involves cutting the log quarter, then the flat side is forced against the cutting knife using hydraulic rams to slice off slabs or a sheet of veneer. These slabs of veneer are generally less than the width of the finished plywood and need to be edge-joined into larger sheets. The rotary cut veneer is also edge-joined when the sheet breaks. The veneer is inspected when dry, and holes are patched to make it ready for the adhesive application step.

Adhesives (qv) used to make plywood are classified as either the exterior adhesive or the lesser quality interior adhesive. The terms relate to the ability of the adhesive to survive exposure to moisture and weather. Phenolic resins (qv) are commonly used as adhesives to make plywood. The difference between interior and exterior phenolic resin adhesive is the filler level. Exterior rated plywood uses higher resin content adhesives. Interior rated plywood uses either highly extended (below 24% resin solids) or protein-based adhesives. The adhesive is applied to the veneer by roll coating, spraying, curtain coating, or foam extrusion.

The adhesive-coated veneers are then stacked in the correct order (thickness and number of plies) to make the desired product and sent to a cold press. The pressure applied by the cold press assures uniform adhesive distribution across the plies and full adhesion later. From the cold press the assembly is moved to a hot press. The hot presses have up to 50 openings between steam heated plates. Depending on the thickness of the plywood being manufactured, one or more (up to three) layers of uncured plywood assemblies are loaded into each opening. The press is closed and pressure of 1.2–1.38 MPa (175–200 psi) and temperatures of 110–166°C are applied for the period of time needed to cure the adhesive. The cured plywood panels are removed

from the hot press and sent past trim saws that trim the panels to final size. A- and B-grade veneer products are sent on for sanding, whereas structural panels with C- and D-grade veneers (lowest quality, the most holes) are not. Following the sanding step, the panels are inspected again and any new defects are patched.

Reconstituted Wood Products. This category includes three general varieties: wood flake board, particle board, and wood fiberboard. The manufacturing processes are similar for all these products except for the size of the wood particles that are glued together.

Wood Flake Boards. This category covers a range of products depending on the size and orientation of the wood flakes used. The earliest product was made in the 1950s using low density wood species, such as aspen and pine, with the flakes bonded together with phenolic resins. Today there are two types of flake board, waferboard and oriented strand board (OSB).

Waferboard is made almost exclusively from aspen wood and the flakes are roughly square in shape, up to 2 in. (5 cm) on a side. They are used for low end structural sheathing applications.

OSB is a product from the 1980s and differs from the waferboards in the shape and orientation of the flakes. Because the flakes are rectangular with the long direction parallel to the grain, they are called strands. Generally, they are S to s-in. (1–2 cm) wide by up to several centimeters long and 1.6 mm thick or less. The strands are laid up in layers with the strand orientation alternating between the long and short direction of the board, much like plywood. It is because of the strand orientation and the strand shape that OSB is considered to have much better structural properties than any of the other reconstituted wood products. It is used in all types of structural sheathing applications, such as roof deck, structural flooring, and structural wall sheathings. A recent application is the manufacture of I-beamlike structures from the sections of OSB, used as replacements for solid wood structural members. These products have the advantage of being more dimensionally stable and uniform, yielding a better building structure.

The 1989 OSB waferboard sales in the United States were about $669 million and increased to 451 × 10^6 m^2 (4.85 billion ft^2 on a 3 8-in. basis) from 18.2 × 10^6 m^2 in 1980. These products represent about 20% of the structural panel market; softwood plywood represents the other 80%.

Particle Boards. Particle board technology was developed in the late 1930s; the first commercial plant began in Germany in 1941. Today particle board products are about 80% of the total wood panel products used in Europe for furniture and construction applications. In the United States particle board did not become a commercial product until the late 1940s, in large part because of the plentiful supply of wood in the United States. A significant feature of particle board is that it uses wood residues like sawdust, edging, and trimming from lumber mills. These wood residues are therefore small in size compared to the waferboard OSB wood particles.

Particle boards are classified into three general categories depending on the density of the board. High density (H) panels are those with a density greater than 849 kg m^3, medium density (M) panels have density between 609 and 849 kg m^3, and low density (L) panels have a density below 609 kg m^3. These three categories are further subdivided by the type of resin that bonds the particles together. Urea–formaldehyde (UF) (see AMINO RESINS AND PLASTICS) bonded panels are called Type I and are for interior application. Phenol–formaldehyde (phenolic) (see PHENOLIC RESINS) bonded panels are called Type II and are used for protected exterior and sheathing applications. Typical applications for the various types of panels are given in Table 3.

Table 3. Particle Board Grade[a] and Applications

Application	Type[b]	Density	Grade[c]
floor underlayment	I	medium	1
shelving	I	medium	1,2,3
countertops	I	medium	2,3
kitchen cabinets	I	medium	1,2
door core	I	low	1
stair treads	I	medium	3
moldings	I	medium	3
wall sheathing	II	medium	1
siding	II	medium	1
combined subfloor underlayment	II	medium	3
high density industrial products	I	high	1,2,3
high density exterior industrial products	II	high	1,2,3

[a] Ref. 1.

[b] Type I UF resin bonded; Type II phenolic resin bonded.

[c] The higher the number, the better the physical properties.

Eighty percent of the markets for particle board are furniture, doors, cabinets, and countertops; floor underlayment is the next significant application with 13%. The total market in 1989 was approximately $930 million.

Wood Fiberboards. The wood particles used to make wood fiberboards are, in fact, individual wood fibers from raw materials including waste woods and other cellulosic materials such as bagasse (sugar cane). The fibers are glued together into a sheet. There are three general types of wood fiberboards, which differ by density. The low density boards have a density below 529 kg m^3, the medium density boards have densities between 529 and 801 kg m^3, and the high density boards have a density greater than 801 kg m^3. The physical properties are influenced by both the adhesive used and the density.

Low density wood fiberboards are usually manufactured at a density of about 448 kg m^3 in a wet process similar to papermaking. The natural binding properties of wood fibers are used and adhesives are not usually added. Starch (qv) and asphalt (qv) are used if a binder is needed for additional strength. This type of product is used in residential sheathing where the manufacturer puts an asphalt coating on the board to protect it from the weather during construction. It is also used as roof insulation or utility board under commercial low slope roofing. Roof insulation boards come either with asphalt, a maximum of 4% incorporated into the board to size the board and help control moisture pick-up, or without asphalt, for use with roofing membranes that are not compatible with asphalt. Finally, low density wood fiberboard is used in residential ceiling tile and panels for aesthetic rather than acoustic properties; they have noise reduction coefficients (NRC) less than 0.5 and are not considered acoustically sound absorbing.

Medium density wood fiberboards (MDF) are semistructural products used mainly in furniture applications (95% of the market). The total shipment of MDF in 1989 was approximately $302 million.

High density wood fiberboards are also known as hardboards. The tempered hardboard manufacturing process was developed by W. H. Mason, founder of the Masonite Corp., in 1924. As a result, hardboards are sometimes referred to as Masonite. There are two types of hardboard, standard and tempered. Standard hardboard has the fibers felted; today this is done by a dry process, but in the past a wet felting process was common. The felted fibers are then pressed to a density between 961 and 104 kg m^3. The strength comes from the consolidation of the fibers under heat and pressure. Tempered hardboard has heat-curing resins impregnated into the standard hardboard before curing. As a result, tempered hardboard is stronger and more moisture-resistant.

Hardboard is available in either 1 8 or j in. (0.32 or 0.63 cm) thicknesses. It is available as peg board with holes punched in it. A significant but declining use has been in interior paneling and exterior siding, and it competes in many applications with thinner OSB and plywood. The U.S. market for hardboard was approximately $669 million or 455 × 10^6 m^2 (4.9 billion ft^2, 1 8 in. basis) in 1989.

Manufacturing Process Overview. Reconstituted wood products have similar manufacturing processes. The first step is to make the particles that will compose the finished product. Wafers and strands are cut from logs, particle board particles are ground from mill scraps, and wood fiberboard fibers are ground and then treated with steam or other methods to break down the natural lignin adhesives holding the fiber together so that

they can be separated into individual fibers. The next step is to mix the wood particles with the resin of choice by a spray and or tumbling process. Urea–formaldehyde (UF) resins commonly were used in the past. However, because of the lack of moisture resistance and the potential for the resins to hydrolyze in the presence of moisture and decompose into urea and formaldehyde, they are not used as much now. Governmental regulations are under development that eliminate the use of UF resin in wood products. This would limit the exposure of the public to formaldehyde, a listed carcinogen, formed by the decomposition of UF resin. Today most wood products use phenol–formaldehyde (phenolic) resins, but urethane-based resins are becoming more common.

After the wood particles are coated with resin, the particles are uniformly distributed into a board by an air laid process. The art of the process is in controlling and getting a uniform distribution of the wood particles by blowing them out onto a collection chain. After forming the board shape it is moved to hot presses where the wood particles are consolidated and the resin cured. From the hot presses the boards move to trim saws where the boards are cut square to their final size. In some cases, the boards are sanded to final thickness and surface smoothness.

Bituminous Products

Bitumen describes a black or dark brown masticlike material that is thermoplastic in nature and softens upon heating. The sources of bitumen are petroleum or coal deposits. The natural product is commonly called gilsonite or pitch, a mineral formed by an old weathered petroleum flow at the surface of the earth that has left behind the larger molecules from the petroleum. A principal source in the past has been Lake Trinidad, a 445,000 m^2 deposit on the island of Trinidad. Bitumen from petroleum or crude oil is called asphalt (qv). It is the material left behind after all the valuable compounds, eg, gasolines, have been distilled out of the crude oil. The amount and quality of asphalt is dependent on the source of the crude oil used in the refining process. Some crude oils have a higher content of asphaltic bitumen left after the distillation process. Bitumen from coal is coal-tar pitch. It remains after the valuable coal oils and tars have been distilled out of the coal tars produced by distractive distillation. Most industrial applications for bitumen products use asphalt or coal-tar pitch because the supply is more uniform and plentiful.

As a construction material, bitumens have principal applications in paving and waterproofing. About 75% of all bitumens are used in paving, and about 20% are used in waterproofing. Of the waterproofing usage, 75% is in roofing applications. Construction applications for natural bitumens are nonexistent and coal-tar application are less than 20% with asphalt being the more important material. The use of coal tar is declining because of its listing as a human carcinogen by the U.S. Government.

Asphalt is not an exact chemical composition but rather a mixture of organic compounds whose nature is dependent on many items (see ASPHALT).

PAVING

The principal use of coal tar in paving is as a seal coat to bitumen paving. Asphalt for paving comes in several forms determined by the intended application, ie, straight asphalts called asphalt cements (AC), asphalt emulsions, cutback asphalts, and road oils.

Asphalt cement represents well over 50% of the total amount of asphalt used in paving. It comes in a range of viscosities from 25 Pa·s (250 P) to 400 Pa·s (4000 P), measured at 60°C. The ASTM D3381 classification system lists the number following the AC as the viscosity of the grade in Pa·s divided by 10, eg, AC 20, a common grade, would have a viscosity of 200 Pa·s (2000 P) at 60°C. ASTM D3381 also lists other physical properties for the various grades. The main application of asphalt cement is as a binder in asphaltic concrete paving, commonly called blacktop. Over 90% of the paved roads in the United States are asphaltic concrete. Asphaltic concrete is a mixture of sand, size-grade rock (2–4 cm) (maximum 1S in., more typically s in.), and asphalt cement. The mixture is heated so that the aggregate is fully coated with asphalt cement and then applied as a uniform layer to the prepared road bed and consolidated under pressure before it cools and sets.

Asphalt cutbacks are asphalts dissolved in a solvent. The choice of solvent and its rate of evaporation determines how quickly the cutback sets up. Cutbacks are used as road sealers and coatings and may be mixed with aggregate and sand for cold patches used to repair minor road damage. The cold patch is put into the hole, consolidated, and allowed to cure; it does not have to be kept hot prior to use. Asphalt cutback is also used as dampproofing by applying a continuous film of asphalt to foundations to retard the flow of vapor water. Current and future limitations on volatile organic compounds (VOCs) found in most organic solvents are responsible for the decreased use of cutback asphalts. It is estimated that all asphalt cutbacks, including those used in roofing, represent about 3–5% of the total asphalt market.

Asphalt emulsions are dispersions of asphalt in water that are stabilized into micelles with either an anionic or cationic surfactant. To manufacture an emulsion, hot asphalt is mixed with water and surfactant in a colloid mill that produces very small particles of asphalt on the order of 3 μm. These small particles of asphalt are prevented from agglomerating into larger particles by a coating of water that is held in place by the surfactant. If the asphalt particles agglomerate, they could settle out of the emulsion. The decision on whether a cationic or anionic surfactant is used depends on the application. Cationic stabilized emulsions are broken, ie, have the asphalt settle out, by contact with metal or silicate materials as well as by evaporation of the water. Since most rocks are silicate-based materials, cationic emulsions are commonly used for subbase stabilization and other similar applications. In contrast, anionic emulsions only set or break by water evaporation; thus an anionic emulsion would be used to make a cold patch compound.

Road oils are very fluid asphalts that are used to keep the dust down on dirt roads. They are only a small part of the asphalt paving market.

ROOFING

Asphalts are used for waterproofing in roofing and as below-grade water barriers applied to foundations. Roofing represents the largest waterproofing application of asphalt, and is commonly classified into low slope roofing and steep slope roofing. The dividing line between steep and low slope is a 2 in. (5 cm) rise per foot (30 cm) of run, also referred to as a 2 in 12 slope. This dividing line generally means the difference between membrane roofing systems versus shingles. However, membrane roofing systems can be used on slope of up to 6 in 12, but shingles are never used under 2 in 12 and generally not used under 4 in 12.

Asphalts in the roofing industry are used as coatings for shingle and roll goods (60%), as mopping asphalts in membrane roofing (20%), as saturants for shingle and roll goods (15%), and as roof coatings (5%). With the exception of saturants and polymer-modified asphalts, the asphalts used in roofing are air-blown or oxidized to increase the softening temperature and penetration so that they will not flow off the roof in hot weather.

The roofing market size is generally reported by building type rather than by roofing material type, ie, residential and commercial. The total roofing market in 1990 was $11.6 billion commercial and $5.1 billion residential for a total of $16.7 billion including labor. Labor is included because in most cases the finished product is produced on site. Of the total, 59% was asphalt roofing with 81% of that based in the residential market and 19% in the commercial markets.

Asphalt Shingles. Asphalt shingles are one of the least expensive roofing options. They represent about 65% of the residential roofing market on a dollar basis, and represent well over 65% on an area basis. The two basic types of asphalt shingles are fiber-glass mat reinforced and organic-felt reinforced. Fiber-glass mat reinforced shingles represent about 85% of the market.

Manufacturing processes are different for each type of reinforcement. Organic felt reinforced shingles have been around since the turn of the century. They start with a blotterlike paper called the felt, which is manufactured from cellulosic materials. Large rolls of the felt are passed through a saturator, ie, a large tank filled with a very soft or low softening point asphalt called saturant. The felt is passed through the saturant numerous times so that the felt picks up about 120% its original weight in saturant and weighs about 0.6 kg m^2. The saturated felt is then run through a roofing line where both sides are coated with a filled asphalt coating. The filled asphalt coating is a hard or high softening point air-blown asphalt blended with 50% or more of a fine filler, commonly ground limestone, that keeps the coating from flowing off the roof and provides a fire rating on fire rated shingles. The top surface has granules of color-coated crushed rock about 3 mm in diameter pressed into it to protect the asphalt from the weather and provide the aesthetics of the shingle. The back coating is treated with sand or other release-type agents to keep the shingles from sticking in the bundles. Lastly an asphaltic adhesive is applied in a strip to seal the tabs of the shingles down on the roof in order to resist wind damage to the finished roof.

Fiber-glass mat reinforced shingles are produced from fine (about 16 μm diameter) glass fibers uniformly dispersed and bonded together with a thermosetting resin. Typically the mat weighs ~0.1 kg m^2. The fiber-glass mat is then run through a coating line where both sides are coated with a filled asphalt coating. The top surface has granules pressed into it, and the back coating is treated with sand or other release-type agents. Lastly an asphaltic adhesive is applied in a strip to seal the tabs of the shingles down on the roof.

The finished shingles, either fiber glass or organic-based, weigh between 9.8 and 16.6 kg m^2 (200–340 lbs 100 sq ft). Standard three-tab shingles are lighter in weight than laminated (two-layer) shingles.

Membrane Roofing. Many of the same types of materials used in membrane roofing are also used in waterproofing applications, because usually a membrane is needed to maintain the waterproofness of the foundation. They are used mainly on large commercial buildings.

Three types of asphalt-based roofing materials are used in the membrane roofing market: built-up roofing (BUR), modified bitumen membranes, and mopping asphalt. BUR represents about 33% of the membrane roofing market and modified bitumen has about 16% of the total market.

Built-Up Roofing. BUR has been used since the late 1800s with a variety of reinforcements. Fiber glass mat and organic felt are the reinforcements used today in the United States; fiber-glass mat is used in most of the material produced. BUR roofing systems use several types of felts or reinforcements between layers of asphalt, to build up the roof. Asphalt is used to provide waterproofing and to glue the layers together; the reinforcement is used to span imperfection in the substrate, and strengthen and stabilize the asphalt against flow and movement. The most common type of felt used to construct roofs is called a ply felt. Additionally, a coated base sheet, or ply sheet coated with filled coating on each side, is used when the roof must be nailed to the substrate rather than adhered. Some roofs may use a cap sheet, or a heavily coated sheet with granules on the top side, for anesthetic reasons.

Typical application of a BUR would be to mop or apply asphalt to a substrate to approximately 1.1 kg m^2 (23 lbs 100 ft^2), or the thickness of a dime. A ply sheet would then be unrolled into the hot asphalt. Additional ply are then mopped in, with each layer offset so that the roof has three or four plies of felt over the entire roof. The amount of offset is calculated by the formula, offset 34 in. (86.4 cm) number of plies. Manufacturers of plies print laying lines on the felts at the correct locations to assist in laying up the roof with the correct offset.

Ply sheet manufacture depends on the type of reinforcement used and is similar to the manufacture of asphalt shingle. Fiber-glass mat reinforced ply sheets represent about 95% of the ply sheet produced in the United States. Fiber-glass mats are coated with a hard unfilled coating asphalt, applied thinly so that only the fiber-glass fibers are coated and the sheet retains its porosity to allow gases to escape during the roof application and the interply asphalt to flow together between layers for a stronger roof construction. The ply sheets are produced 3 ft (91 cm) wide in rolls that cover 500 ft^2 (46.5 m^2) with laying lines applied to the top side of the sheets.

Organic ply sheets are manufactured from 3 ft (91 cm) wide organic felts, saturated with soft asphalt, that cover 400 ft^2 (37 m^2). Laying lines are applied to the top side of the ply sheets, and the felts are perforated about 2 to 4 in. (5 to 10 cm) on center to permit the gases to escape during the roof construction process.

Modified Bitumen Membranes. These membranes were developed in Europe during the late 1950s and have been used in the United States since the late 1970s. There are two basic types of modified asphalts and two types of reinforcement used in the membranes. The two polymeric modifiers used are atactic polypropylene (APP) and styrene–butadiene–styrene (SBS). APP is a thermoplastic polymer, whereas SBS is an elastomer (see ELASTOMERS, THERMOPLASTIC ELASTOMERS). These modified asphalts have very different physical properties that affect the reinforcements used.

Atactic polypropylene (APP) is a by-product of the crystalline or high density polypropylene manufacturing process (see OLEFIN POLYMERS). Its use as a modifier for asphalt was developed in Italy. The addition of APP to asphalt gives a uniform matrix that increases the flexibility of the asphalt at both high and low temperature and improves water penetration resistance as well as ultraviolet resistance. The addition of between 20 and 35% APP increases the softening point of the asphalt mixture to about 149°C, which is high enough to prevent slippage on the rooftop. This higher temperature does not allow fusion between the APP coating and the mopping asphalt to take place or a bond to develop between the mopping asphalt and the membrane. For this reason, APP membranes are generally installed using a gas-fired torch to melt the thick back coating of APP-modified asphalt; thus it is used as the mopping or interply asphalt. This application technique is valuable when it is difficult to get hot asphalt to the rooftop. Even though the ultraviolet resistance is improved over nonpolymer modified asphalt, most manufacturers recommend that APP membranes have a coating or other protective surface applied to protect the bitumen from ultraviolet radiation damage. Most APP membranes use a nonwoven polyester mat as the reinforcement in the membrane. This increases the flexibility of the sheet. Also, APP membrane systems generally include a basesheet or other underlayment sheet, making them a minimum of a two-ply system, which provides a second layer of protection against leaks.

Styrene–butadiene–styrene modified bitumen is an elastomeric material mixed into an asphalt between 10 and 15%. By using high energy mixing, the SBS is uniformly dispersed throughout the asphalt to form a network, referred to as phase reversal because the minor component's (SBS) physical properties are displayed by the final mixture. A properly formulated SBS asphalt blend has an elongation of 100% or greater and is flexible down to temperatures below 6°C.

SBS membrane systems are generally installed in hot asphalt but can be installed using a torch like APP products or in some cold application cement systems. Like APP systems, they are generally installed in multiple layers. The underlayment layers are generally standard BUR felts or basesheets. SBS membrane sheets can also be formulated to be self-adhering. These products are no longer used in membrane applications but are used as ice and water dam materials on the eaves under shingle roofs in cold climates.

Both fiber-glass mats and polyester mats are used either individually or combined in SBS membrane sheets. Because of the elastomeric properties of the asphalt, SBS sheets have developed a reputation as being very tough and abuse-resistant. However, they do not have any better ultraviolet resistance than conventional asphalts, so most of the SBS sheets come with a factory-applied surfacing of granules.

Mopping Asphalt. When it was discovered in the late 1800s that oxidizing asphalt gave improved properties of tenacity, less brittleness, and less changes with temperature, the asphalt roofing industry was off and running. Mopping asphalts are air-blown or oxidized asphalts classified in ASTM D312 by softening point and penetration into the four types described below.

Type I asphalt is the softest type of mopping asphalt with softening points between 68°C and with penetration at 25°C between 18 and 50 mm 10. It is for roof slopes of less the j in. per ft (0.25 per 12). It is also called dead level asphalt and is not commonly used today because of the porosity of the fiber-glass ply felts and the industry recommendation that roof slope a minimum of j in. per ft.

Type II asphalt is the second most common type of asphalt used because it offers the best compromise between softness and weatherability and lack of fl °C with penetration at 25°C between 18 and 40 mm 10. It is for roof slopes less than 1 per 12 and is also called flat asphalt. If Type II asphalt is used on the roof, it cannot be used on flashings.

Type III asphalt is the most common type of asphalt used. It has softening points between 85 and 93°C with penetration at 25°C between 15 and 35 mm 10. It is for roof slopes between j (0.63 cm) and 3 in. (7.6 cm) per ft (30.5 cm), ie, 0.25–3 per 12 and is also called steep asphalt or 190 asphalt, in reference to its nominal softening point (190°F 88°C). Type III asphalt can be used on flashings, except in the hottest climates.

Type IV asphalt is not common except in very hot climates. It has softening points between 96 and 107°C with penetration at 25°C between 12 and 25 mm 10. It is for roof slopes greater than 1 per 12, and is also called special steep asphalt. Type IV asphalt is used on flashings and in hot climates to keep the roofing system from sliding off the roof in hot weather.

Coal Tar. In roofing, coal tar is used as mopping bitumen in between 15 and 20% of the BUR roofs installed. Coal-tar pitch and asphalt are considered incompatible and should not be mixed. If mixed, an oily exudate is formed that plasticizes the bitumen, and the mixture remains soft and does not weather well. For this reason, if coal tar is used in BUR systems the felts must be coal-tar saturated. There has been some success using asphalt-coated fiber-glass mat felts with coal-tar pitch. However, this has only been done for a limited number of years so the actual compatibility is not fully known.

Gypsum Products

Gypsum *[13397-24-5]*, $CaSO_4 \cdot 2H_2O$, is a naturally occurring mineral found mainly in the western United States and eastern Canada (see CALCIUM COMPOUNDS, CALCIUM SULFATE). The purer deposits require only minimal beneficiation to get a product pure enough for commercial applications. Other

deposits require cleaning to remove clay and other impurities.

The principal use of gypsum in construction is as a wall finishing material. The manufacturing process requires that the gypsum be partially dehydrated to the hemihydrate *[10034-76-1]*, $CaSO_4 \cdot S\ H_2O$, commonly known as plaster of paris. When mixed with water the hemihydrate dissolves and the gypsum precipitates out as the interlocking crystals that make gypsum a hard monolithic material. The reaction is rapid, exothermic, and autocatalyzed by gypsum itself. For some applications the reaction is slowed by the addition of protein materials to the hemihydrate–water mixture.

In the United States, over 90% of the gypsum products sold are as gypsum board. Gypsum board is used as an interior wall surfacing in both residential and nonresidential construction and is referred to as drywall to differentiate it from the older wet plaster walls. The board is composed of a core of gypsum attached to a facing of heavy paper and is attached to the framing members using either nails or screws made especially for installing drywall. The joints between the board are cosmeticly treated with a reinforcing tape and joint compound composed of mineral fillers and a thermosetting resin emulsion; some flow control and viscosity modifiers may be added to help get an easy, smooth-applying system. The reinforcing tape, either a 5-cm wide paper or fiber mesh, is embedded into the joint compound, allowed to dry, and then topped with a second or third coat of joint compound to obtain a smooth surface. To help in the taping process most board is produced with a tapered edge on the long edges.

The standard sized sheets are four ft (1.22 m) wide and from 8 to 16 ft long. Sheets are available in thicknesses from j up to 1 in. (0.63 to 2.5 cm), but the most common thicknesses are S and 5 8 in. (1.3 and 1.6 cm). There are special products for bathrooms, such as moisture-resistant board (3% of market) and sheathing applications (2% of market), but the vast majority of the product sold is either standard board (60% of market) or the fire-rated Type X board (29% of market). Type X (1.6 cm thick) is the basis of most of the one-hour fire walls in buildings built since the 1960s.

The total market for gypsum product in 1989 was approximately $2.47 billion. Of this amount, 70% was sold by the three largest producers.

Gypsum Board Manufacture. The manufacture process begins with the mining of the gypsum rock from open-pit mines. After mining, the rock is crushed and cleaned to an 85% purity level or better. In a process called calcination, the powdered gypsum is heated to dehydrate the gypsum to the hemihydrate. The calcination process is carried out as either a continuous process, ie, flash calcining, or by the older batch-type process, ie, kettles process. The calcined gypsum or hemihydrate, also called stucco, is ready to be mixed with water, soap foam to reduce the core density, accelerator or retarders to adjust the reaction rate, and other additives used by the manufacturer. Other additives include starch to help with the core facer bond, vermiculite and glass fibers in the Type X product, asphalt–wax emulsions in moisture-resistant products, and pulped waste paper for added strength. These ingredients are all mixed with a high speed mixer and the resultant mix dumped out onto the face paper, which is prefolded so it can wrap around to the back side of the core. The backing paper is brought down and bonded to the folded over edges of the face paper, and the whole assembly is sized for thickness by a roller and doctor bar.

Gypsum board paper is a special three-ply paper manufactured from repulped newspapers. The face paper or cream face has the ply against the core unsized so that the gypsum crystals can grow into it, as this is the principal form of bonding between the core and facers. The middle ply is sized and the outer ply is more heavily sized and treated to control paint absorption. For the completed gypsum board system to work, the joint treatment and paper must absorb paint at the same rate.

The back paper or gray back is also a three-ply paper very similar in construction to the face paper, except it is approximately 4 ft (1.2 m) wide and the outside surface is not treated for paint absorption like the cream face.

To produce tapered edge wallboard, tapered belts are added to the rubber conveyor belt that carries and supports the board while the gypsum core sets up, typically in about four minutes.

After the core sets up, but while it is still wet, the board is cut to rough length, flipped over so that it goes through the oven on the back side, and sent in to dry. The drying step must be done with care otherwise the board will dry too fast, releasing steam faster than it can escape from the facers and blow the facers off the core. In addition, if the board is heated too much the gypsum crystals that have grown into the facer will be calcined, thus destroying the bond.

After exiting the oven, the boards are cut to final length, packaged face to face, and the four-foot edge is taped making a "book." From there it is ready for shipment to the customers.

Portland Cement

Portland cement is the most widely used construction material in the world (see CEMENT), especially in Third World nations, because of its availability, ease of use, and versatility. Estimated 1989 worldwide production is almost 1.12 billion metric tons. The United States represented 71.2 million metric tons, ie, fourth, behind China (207 million metric tons), the former USSR (140 million metric tons), and Japan (82 million metric tons). Spain is tenth with 27 million tons. The top 10 world producers of Portland cement account for just under 43% of the total production.

Portland cement is classified as a hydraulic cement, ie, it sets or cures in the presence of water. The term Portland comes from its inventor, Joseph Aspdin, who in 1824 obtained a patent for the combination of materials referred to today as Portland cement. He named it after a grayish colored, natural limestone quarried on the Isle of Portland, which his cured mixture resembled. Other types of hydraulic cements based on calcium materials were known for many centuries before this, going back to Roman times. Portland cement is not an exact composition but rather a range of compositions, which obtain the desired final properties. The compounds that make up Portland cements are calcium silicates, calcium aluminates, and calcium aluminoferrites (see).

Portland cement is not useful by itself to the construction industry. Its value is in the resultant concrete in which it is used as a binder. Concrete is a mixture of smaller particles that coalesce into a solid mass, and the typical particles in a Portland cement concrete are aggregates of rock and sand. In general, the larger the aggregate size the stronger the Portland cement concrete. The crush and shear resistance of the aggregate, and the ratio of Portland cement to sand and aggregate are important to the strength of Portland cement concretes, with higher Portland cement levels yielding stronger concrete.

PORTLAND CEMENT MANUFACTURE

Portland cement is manufactured by two basic processes, the wet process and the dry process. The dry process uses approximately 25% less energy per ton of Portland cement and is used to produce about 68% of the U.S. Portland cement. Both processes start by mixing selected raw materials, crushed and or milled to approximately s in. (1.9 cm) diameter, in the correct ratios to give the final desired chemical composition.

The choice of selected raw materials is very wide, but they must provide calcium oxide (lime), iron oxide *[1309-37-1]*, silica, and aluminum oxide (alumina). Examples of the calcereous (calcium oxide) sources are calcium carbonate minerals (aragonite *[14791-73-2]*, calcite *[13397-26-7]*, limestone *[1317-65-3]*, or marl), seashells, or shale. Examples of argillaceous (silica and alumina) sources are clays, fly ash, marl, shale, and sand. The iron oxide commonly comes from iron ore, clays, or mill scale. Some raw materials supply more than one ingredient, and the mixture of raw materials is a function of their chemical composition, as determined by cost and availability.

In the wet process, the correct ratios of raw materials are ground up and mixed in a water slurry to a uniform intimate mixture, which is sent to the kiln where the chemical reactions take place to form the Portland cement composition. In contrast the dry process does all the grinding and blending on dry materials. Following the grinding and blending step, both wet and dry processes are very similar. The chemical transformations take place at high temperatures in a rotating kiln, which has large sloped rotating tubes whose length and diameter determine the production rate.

Kilns in the United States range in size from about 50,000 metric tons per year to 1.36 million metric tons per year of production. The ground raw materials are fed into the upper end of the kiln, while the lower end is fired to temperatures of 1425 to 1650°C using either coal, oil, or gas; approximately 85% of the production capacity is coal fired. The ground raw materials are moved countercurrent to the hot exhaust gases by the slope and rotation of the kiln. While moving down the kiln, the raw materials have some components driven off as gases whereas the remaining components are combined to form a material with new chemical and physical properties called clinker. Clinker is a grayish black marblelike pellet approximately 1 cm in diameter. It is collected, cooled, and then ground to a fine powder with a small amount of gypsum to regulate the setting time of the cement. The grinding produces a very fine powder with 90% finer than 75 μm and 80% finer than 50 μm. This is Portland cement.

The manufacture of Portland cement is very energy intensive. It has been identified by the Department of Commerce as one of the six most energy

intensive industries per ton of product. Portland cement is also very heavy, having a specific gravity of 3.15; thus it is not shipped very far. This accounts for the presence of over 100 plants around the United States. Industry data show that the average shipping distance for Portland cement is approximately 176 km.

TYPES OF PORTLAND CEMENT

ASTM C150 Standard Specification for Portland cement defines eight types of Portland cement produced to meet the performance requirements of different applications.

Type I (Normal). This is the general purpose Portland cement used for all applications where special properties are not needed. Common applications include concretes for paving, building floors, roof decks, reinforced concrete buildings, pipes, tanks, bridges, and other precast concrete products. In 1989 Type I and Type II accounted for over 92% of the Portland cement produced in U.S. plants. Exact data are not available that separate Type I and Type II Portland cement, but it can be assumed that Type I production was much greater than Type II.

Type II (Moderate Sulfate Resistance). This Portland cement is used where exposure to sulfate attack at concentrations between 150 and 1500 ppm is possible, such as drainage structures where higher than normal sulfate exists in ground water. Type II Portland cement releases about 80 to 85% of the heat of hydration of Type I Portland cement during the first seven days and is used where slightly lower than normal heats of hydration are needed, such as in structures with considerable mass, ie, large piers and retaining walls. This keeps the internal heat on the poured structure down, increasing its final strength. Type II Portland cement is also often used in warm weather construction.

Type III (High Early Strength). Type III Portland cement provides higher strength earlier (one week) than does Type I (four weeks) Portland cement, but it generally does not achieve the same final strength as Type I. Chemically, Type III is the same as Type I except it is ground finer. Type III is used where it is necessary to remove the forms quickly or in cold weather where it is desirable to have less time under controlled temperature conditions. It releases about 150% of the heat of hydration of Type I Portland cement during the first seven days. Production of Type III Portland cement in the United States in 1989 was approximately 3.7% of the total Portland cement production.

Type IV (Low Heat of Hydration). Type IV is used where the rate and amount of heat generated from hydration have to be minimized, ie, large dams. Compared to Type I, Type IV Portland cement has only about 40 to 60% of the heat of hydration during the first seven days and cures at a slower rate. In large structures such as dams where the heat of hydration cannot be readily released from the core of the structure, the concrete may cure at an elevated temperature, and thermal stresses can build up in the structure because of nonuniform cooling that weakens the structure. U.S. production of Type IV Portland cement is less than 1%.

Type V (High Sulfate Resistance). Type V Portland cement is used in concrete exposed to severe sulfate attack of 1,500 to 10,000 ppm. Low concentrations of tricalcium aluminate *[12042-78-3]* give Type V its sulfate resistance. The sulfate resistance is improved with air entrainment and low water to cement ratios in the wet concrete. U.S. production of Type V Portland cement in 1989 was 0.9% of the total Portland cement production.

Air Entraining Portland Cement. Types IA, IIA, and IIIA Portland cements are similar to the standard counterparts, but they are air entraining. During the grinding process, small amounts of air entraining agents are coground with the clinker and form tiny, well-distributed, completely separated, air bubbles during the concrete mixing process at a rate of 6% or more by volume. The air bubbles impart improved freeze–thaw resistance and improved slump or flow at the same water content. Air entrainment can also be obtained with the use of admixes designed to entrain air when standard Portland cements are used.

Other Types of Portland Cements. *White Portland cement* is standard Type I or III Portland cement with raw materials selected and controlled to have negligible amounts of iron and manganese oxides, which impart the gray color. The white Portland cement is used in decorative and architectural applications like precast curtain walls, terrazzo surfaces, stucco, tile grout, and decorative concrete.

Blended hydraulic cements are used to conserve energy. They are intimate and uniform blends of fine materials such as Portland cement, ground blast furnace slag, fly ash, and other pozzolans, ie, fine, reactive silica sources. ASTM C595 lists five classes or types.

Type IS	Portland cement and blast furnace slag cement
Type IP or P	Portland cement and pozzolan cement
Type I(PM)	pozzolan and modified Portland cement
Type S	slag cement
Type I(SM)	slag and modified Portland cement

Masonry cements are hydraulic cements designed to have improved workability for use in mortar for masonry construction. The standards are given in ASTM C91.

Expansive cements are hydraulic cements designed to expand rather than shrink on curing, as do standard Portland cements. They are defined in ASTM C845 and are used to control and reduce shrinkage cracks in large poured-in place structures.

Plastic cements are hydraulic cements that have plasticizing agents added to Portland cement during the grinding operation to make them flow better. The primary use for plastic cements is in plasters and stucco.

PORTLAND CEMENT CHEMISTRY

The chemistry of Portland cement is not completely understood. During the burning or kiln process, the calcium oxide *[1305-78-8]* combines with the acidic compounds in the clinker to form four principal compounds that make up approximately 90% of Portland cement by weight. These materials are tricalcium silicate *[12168-85-3]*, $3CaO{-}SiO_2$; dicalcium silicate *[10034-77-2]*, $2CaO{-}SiO_2$; tricalcium aluminate *[12042-78-3]*, $3CaO{-}Al_2O_3$; and tetracalcium aluminoferrite *[12612-16-7]*, $4CaO{-}Al_2O_3{-}Fe_2O_3$. When these four materials are mixed with water they hydrate and form other materials that are the infrastructure of the hardened Portland cement paste in concrete. Tri- and dicalcium silicates, which make up about 75% of the Portland cement, react with the water to form calcium hydroxide *[1305-62-0]* and calcium silicate hydrate, $3CaO \cdot 2SiO_2 \cdot 3H_2O$, also known as tobermorite gel. In the hydrated Portland cement, tobermorite gel is about 50% by weight and calcium hydroxide, $Ca(OH)_2$, is 25%. It is the tobermorite gel that gives the cured cement its strength and other properties. The hydration of tricalcium aluminate also involves reactions with the calcium hydroxide released by the calcium silicate hydration to form tetracalcium aluminate hydrate, $3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 12H_2O$. Lastly, the calcium aluminoferrite hydrates to form calcium aluminoferrite hydrate, $6CaO \cdot Al_2O_3 \cdot Fe_2O_3 \cdot 12H_2O$.

The properties of cured Portland cement are affected by these four constituents of the manufactured Portland cement. Tricalcium silicate hydrates and hardens rapidly, giving rise to the initial set and early strength. Increased concentrations of tricalcium silicate causes an increase in the early strength of Portland cement concretes. Dicalcium silicate hydrates and hardens more slowly, giving the cured concrete its strength increases beyond one week.

Tricalcium aluminate is the principal exothermic reactor in Portland cement giving rise to the heat release during the first couple of days and contributing some to the early strength. Gypsum added during grinding slows down the hydration reaction of tricalcium aluminate, thus controlling the overall reaction rates.

$$3CaO \cdot Al_2O_3 + 10H_2O + \underset{\text{gypsum}}{CaSO_4 \cdot 2H_2O} \rightarrow 3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$$

Low tricalcium aluminate improves sulfate resistance.

Tetracalcium aluminoferrite acts as a processing aid by reducing the clinkering temperature. It hydrates rapidly but does little for any performance property of the cured concrete. It does, however, cause most of the color effects in the cured concrete.

APPLICATIONS

The primary market for Portland cement is in building construction, which historically takes approximately 65% of all Portland cement sold. Forty-five percent of the construction market goes for residential construction and 38% goes for commercial construction. These markets use Portland cement for concrete foundations and structural and precast products. Precast products generally have some form of reinforcement in them, either steel reinforcing rods or more generally pretension steel cables that are tensioned prior to pouring the concrete. After the concrete cures, the tension is released and the cables attempt to contract, thus putting the concrete under compression. Portland cement concretes perform very well in compression but poorly in tension. With the addition of steel reinforcing the concrete has good performance in both compression and tension. A newer twist on this concept is post-tensioning where the cable is tensioned and maintained under tension after the concrete sets.

For special high strength applications, ie, up to 69 MPa (10,000 psi), special formulations of Portland cement concretes have been developed. These are based on the use of chemical and mineral admixtures. The typical mineral admixtures are fumed silica and other pozzolanics. The chemical admixtures are generally chemicals termed superplasticizers that allow very low water to cement ratios, ie, between 0.4 and 0.25, and reduce the amount of water needed to provide plasticity or flow to the concrete. Public works applications take just under 32% of the total Portland cement market; streets and highways represent 68% of this usage, and water and waste account for 23%.

Bricks

Bricks are the oldest manufactured building material in use. Sun-dried bricks were manufactured as early as 6000 BC, and fired bricks were used during the Middle Ages. Today's bricks differ very little except in the efficiency of manufacture; they are still made from clay or shale, a clay-based sedimentary rock that is kiln-fired.

Manufacturing Process. There are three processes used to make bricks. All three start with clay that has been milled and screened to remove coarse materials and impurities. The clay used must have enough plasticity when mixed with water to allow molding and have enough wet and dry tensile strength to maintain the brick shape after forming. Water is added to the prepared clay in an amount appropriate for the brickmaking process that will be used. The clay and water mixture is then kneaded with rotating knifes to form a plastic mass, which is then molded into a brick shape by one of the three processes.

The stiff-mud process is the most common method in use. In this process, the clay–water mixture is extruded into a long ribbon of the correct cross-section size. The water content is typically 12 to 15% by weight. Very often before extruding, the clay water mixture is subjected to a vacuum of 50–97 kPa (375 to 725 mm Hg). This step removes air holes and bubbles, thus increasing the strength of the finished brick and the workability of the clay–water mixture. The ribbon is cut to individual brick lengths by rotating wire knifes and the raw bricks stacked for drying and burning, ie, firing.

The soft-mud process is used to make handmade brick. More water is added to the clay to make a thinner paste, typically about 20 to 30% by weight of water. The resulting slurry is packed into molds that have a sand or water coating on them that acts as a release agent. The wet brick shapes are removed from the molds when they have set up enough to handle and are then stacked for drying and burning.

The dry-press process is used to make good quality face brick, ie, brick used on exposed walls. Very little water is added to the clay, less than 10% by weight. This is only enough water to make the clay damp. The damp clay is then pressed into molds under pressures of 3.4 to 10.3 MPa (500 to 1500 psi). The damp brick shapes are removed from the molds when they have set up enough to handle and are stacked for drying and burning.

Following the forming process, the bricks are dried in drying rooms where hot air (38 to 204°C) is circulated. The bricks must be dried slowly to prevent large amounts of shrinkage and cracking. Drying times depend on the condition and the moisture content on the brick shapes, but normally range from 24 to 48 h.

After drying, the bricks are put into a kiln where the temperature is raised slowly to between 870 and 1316°C or higher depending on the temperature needed to fuse the clay. With the clay particles partially melted and fused together, the brick is a ceramic material with excellent strength and fire resistance.

There are two basic types of kilns used, the tunnel kiln and the periodic kiln. The tunnel kiln has the highest production rate and uses cars to carry the dried brick through the firing or burning process. Tunnel kilns can produce from 40 to 80 million bricks a year each. The periodic kiln is a batch-type kiln that is loaded, run through the cycles, and then emptied. Because of the firing process, brick manufacture requires much energy, which represents approximately 35% of the total manufacturing cost.

There are six stages of firing. Water-smoking is the evaporation of free water, done at temperatures up to 204°C. Dehydration removes the chemically combined water from the clay structure at temperatures between 149 and 982°C. During oxidation the iron oxide is oxidized to ferrous oxide, which gives a red color. It is done between 538 and 982°C. Vitrification fuses the clay particles together at temperatures between 871 and 1316°C. Flashing runs the kiln with a reducing atmosphere at a temperature below the vitrification temperature to produce color variation. Reduced iron oxides are purple in color. Cooling brings the hot brick down to near ambient temperature slowly, over 48 to 72 h, to keep the bricks from cracking and changing color.

Bricks are available with several types of textures: roughened, smooth, or glazed with a glasslike glaze coating applied to its face. In the United States 94% of the production is face brick used for the outer surface of a wall. The bulk of the remainder is backing or common brick used behind face brick.

The brick industry in the United States is comprised of approximately 120 companies that operate 236 plants across the country. Their sales in 1989 were $1.2 billion, with 64% in residential construction, 31% in commercial construction, and 5% for nonbuilding usage. Brick was used on 31% of new commercial buildings and 17% of new homes built.

Glass

Glass (qv) was not used until the early 1800s as a construction material. Prior to the 1930s the only use of glass for construction was in windows. In the mid-1930s, fibrous glass was developed, which is widely used as an insulation material.

The term glass has two meanings, ie, the material and a state of matter. The glassy or vitreous condition is where the atoms of the material have a random orientation. This amorphous or noncrystalline nature leads to physical properties typical of the product called glass, including unpredictable breaks, no sharp melting temperature, and no heat of fusion.

The products called glass are in the glassy state and are made mainly from silica *[7631-86-9]* (silicon oxide *[10097-28-6]*, SiO_2). Sodium oxide *[1312-59-3]*, Na_2O, and calcium oxide *[1305-78-8]*, CaO, are commonly added up to 30% or more in combination. Sodium oxide is added to reduce the viscosity or melting temperature of the silica, whereas calcium oxide gives the glass durability against water attack. Glasses can contain a wide range of oxides depending on the application and properties needed of the glass. Examples of other oxides include the oxides of boron, aluminum, potassium, magnesium, lead, barium, zinc, and lithium.

Sand is the common silica source, but the sand must have only minor impurities in order to make good quality, clear glass. A common source for sodium oxide is sodium carbonate *[497-19-8]*, Na_2CO_3, from soda ash. Upon heating in the glass furnace it forms the oxide. Calcium oxide comes from limestone, which when burnt becomes lime *[1305-78-8]*, CaO. Alumina *[1344-28-1]* commonly comes from feldspar *[68476-25-5]*, which is an alumina silicate rock. Boron oxide *[1303-86-2]* is obtained from borax, sodium tetraborate *[1330-43-4]*, $Na_2B_4O_7 \cdot 10H_2O$. Other oxides generally are not used in large amounts or at all in glass construction materials.

Uses of glass in construction products fit into three categories: flat glass (window glass); fibrous glass; and specialty glass products. Each is made by different processes and has different applications.

Flat Glass. Flat glass is widely used in applications other than construction, such as automotive glass, etc, but approximately 57% of the flat glass is used in construction applications, mainly as windows. This represents about $2.2 billion worth of material in 1989 for the United States.

The float glass manufacturing process was developed by Pilkington Brothers Ltd. of England in 1959. It starts with a large continuous tank furnace

in which finely ground glass raw materials are added at one end and molten glass is removed at the other end. Typically the tank is heated with natural gas to melt the glass. The glass must be retained in the tank after it melts for a period of time to allow the materials to fully intermingle and form good quality glass. The molten glass is then fed onto a tank of molten tin called a float bath. The temperature of the molten tin is carefully controlled so that any imperfections in the bottom surface of the glass can be melted out. Since the melting temperature of tin is lower than that of glass, the glass starts to solidify on the tin, incorporating the smooth surface of the molten tin on its underside and a smooth surface on the air side. The glass sheet is then annealed, ie, heated below its melting temperature, with controlled cooling to relieve stresses. The glass is then cut into smaller pieces.

Fibrous Glass. Fibrous glass is manufactured in two different forms, very fine intermingled fibers called insulation fibrous glass for insulation and fine but coarser fibers called continuous or textile fibers for reinforcement and other textile applications. Both products have construction related applications.

Insulation Fibrous Glass. Most insulation fibrous glass is manufactured by a rotary process. The glass is melted in either continuous tank furnaces or electric furnaces. The molten glass is directed to a rapidly spinning disk with a multitude of fine holes in its rim, which operates very much like a cotton candy machine in that the molten glass is extruded out of the hole by centrifugal force. The fine fibers are further attenuated or drawn finer by jets of air or flame. Fibers typically have average diameters of 3 to 6 μm. The fibers are immediately coated with either a binder or a dedusting agent and collected into the familiar insulation batt. Most insulation fibrous glass is coated with a phenol–formaldehydebased resin that is cured in an oven. The density of the final product depends on the amount of compression done on the blanket in the curing oven and the needs of the application for which the product is manufactured. Densities of less than 0.0624 kg m^3 to over 0.624 kg m^3 can easily be made. Besides wall insulation batts, fibrous glass is used to insulate and make air ducts and insulate pipes and equipment. Fibrous glass is not only used to insulate against heat flow but is also commonly used for sound absorption and control applications.

Fibrous glass insulation products require energy in their manufacture. However, it has been estimated that they save approximately 20 J per year for each joule used in production. In the United States in 1980, approximately $1.9 billion of insulation fibrous glass was sold, which is over 1.4 billion kg.

Continuous Filament Fibrous Glass. This glass is manufactured by drawing molten glass out of a bushing, which is manufactured from platinum or platinum alloys and contains many holes. The diameter of the continuous filament fibrous glass is dependent on the rate that the glass is pulled from the holes of the bushing. Immediately after coming out of the bushing the fibers are coated with either a chemical coating called a size, or water to protect the glass surface from damage. Continuous filament fibrous glass is commonly manufactured in fiber diameters between 10 and 16 μm.

The largest market, approximately 30% in 1989, for continuous filament fibrous glass in the United States construction markets is as fiber-glass mat used to make roofing materials. This is manufactured on a wet forming machine similar to equipment used to make paper or polymer nonwovens. Other uses of fiber glass mat include backing for vinyl flooring and wallpaper. The other market for continuous filament fibrous glass products in the construction market is as fiberglass reinforced polymer materials like bathtubs and shower stalls (see REINFORCED PLASTICS).

Specialty Glass Products. Foam glass insulation and glass building blocks are two specialty glass products with construction applications.

Foam glass was invented in 1942 and is a closed cell glass material blown with hydrogen sulfide gas. It is used in industrial and roof insulation applications where its extremely low moisture permeability is valuable.

Glass building blocks are manufactured by molding both sides of the block, then fusing the two sides together to form the block. They are used to let light into buildings while still having some insulation value because of the dead air space inside the block.

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PLASTIC

Plastics are playing an increasingly important role in the building materials market. From 1980 to 1990 the growth in total plastics volume consumed for building and construction applications averaged 6% annually, nearly two times the average gross national product (GNP) growth over the same period. Whereas plastics were first employed for decorative and nonstructural purposes, today they are used increasingly in functional and structural applications.

Throughout the 1990s, plastics consumption in building materials is forecast to grow at 4–5% average annual rate. Contributing to this growth will be advances in do-it-yourself and professional remodeling products employing plastics, overall growth in the renovation and home remodeling markets, plus the increased penetration of plastics at the expense of traditional materials in building products because of their superior strength in weight performance, corrosion resistance, environmental stability, lower cost, insulation properties, and ability to fabricate complex designs into a single part, ie, low labor assembly intensity. On the other hand, the overall growth of plastics in building materials will be somewhat limited by concerns over their flammability and smoke toxicity, public perception of their negative environmental impact, resistance by the conservative construction industry in adopting new materials, and competitive actions by producers of traditional building materials, such as wood, concrete, glass, and metal seeking to defend their market positions.

Polymers and Properties

The physical properties of plastics that are important in building materials are the glass-transition or melt temperature, ease of processing, as indicated by the temperatures and pressures needed for molding, heat deflection temperature, uv stability, tensile and impact strength, oxidative degradation, creep set, fatigue, and elongation. Density, thermal conductivity, and fire resistance are important for foams. The most important plastics building materials are described below, and their physical properties are summarized in Table 1.

Table 1. Physical Properties of Selected Plastic Building Material[a]

Properties of plastic[b]	LDPE	LLDPE	HDPE	PP	PVC (flexible)	PS	ABS	Polyacrylic (glazing)	Polycarbonate (glazing)	Epoxy (mineral filled)	Acetal homopolymer
melting point, °C	96–115	122–124	130–137	160–175							175–181
glass-transition temp T_g, °C					75–105	74–105	110–125	90–105	140–150		
injection molding temperature, °C	150–232	177–260	176–274	204–288	160–196	177–260	193–260	163–260	270–295		193–243
injection molding pressure, MPa[c]	34–103	34–103	83–103	69–138	7–14	34–138	55–172	34–138	55–140		69–136
tensile strength, MPa[c]	8–31	13–26	22–31	31–41	7–24	35–52	22–55	46–76	65	48–90	67
elongation, %	100–650	100–965	10–1200	500–600	200–400	1–5	2–25	2–10	110	1–3	25–75
Izod impact strength, J/m[d]	no break	no break	21–213	21–64	varies widely	18–24	74–640	16–32	750	16–24	64–123
heat-deflection temperature, °C	40–44		80–91	107–121		66–96	96–118	80–107	138		

Properties of laminates	Melamine	Phenolic, woodbase	Polyester, glass-filled
laminating temperature, °C	145–165	150–160	RT-150
laminating press, MPa[c]	3.5–12	7–14	0–3.5
tensile strength, MPa[c]	69–172	110–220	69–172
Izod impact strength, J/m[d]	16–80	214–427	240–1500
heat-deflection temperature, °C	105	90	

Properties of foams	Polyurethane	Polyisocyanurate	PS board	PS expandable beads
density, kg/m^3	14–42	24–56	24–80	13–15
maximum service temperature, °C	80–170	150	75–80	75–80
thermal conductivity, W/(m·K)	0.0125–0.034	0.012–0.02	0.023–0.034	0.03
fire resistance[e]	HF-1		HF-1	HF-1

[a] Ref. 1.

[b] LDPE = low density polyethylene; LLDPE = linear low density polyethylene; HDPE = high density polyethylene; PP = polypropylene; PVC = polyvinyl chloride; PS = polystyrene; ABS = polyacrylonitrile-butadiene-styrene.

[c] To convert MPa to psi, multiply by 145.

[d] To convert J/m to ft-lbf/in., divide by 53.38 (see ASTM D256).

[e] HF-1 = UL Standard 94 for Foam Plastics.

Low and Linear Low Density Polyethylene. Low density polyethylene (LDPE), 0.91–0.94 g cm^3, is a thermoplastic that melts at ca 115°C. It is insoluble at room temperature but dissolves in various solvents when molten. During polymerization, side reactions cause chain branching. The degree and kind of branching can be controlled to a considerable extent and the properties of the polymer correspondingly modified. Branching decreases crystallinity and density and increases the molecular weight distribution. A decrease in crystallinity decreases hardness, stiffness, melt temperature, and chemical resistance; it increases toughness, flexibility, and permeability. An increase in molecular weight distribution facilitates processing but reduces strength, toughness, and resistance to environmental stress-cracking. The average molecular weight also affects these properties. Increasing molecular weight increases the strength, toughness, and melt temperature but decreases the ease of processing and the melt index.

Linear low density polyethylene (LLDPE), 0.91–0.94 g cm^3, is a copolymer of ethylene with an alpha-olefin such as 1-butene, 1-hexene, 1-octene, and 4-methyl 1-pentene. Polymerization to LLDPE is frequently carried out in the gas phase, eg, Union Carbide UNIPOL and British Petroleum gas-phase technologies, employing a catalyst. Linear low density polyethylenes provide additional melt strength, toughness, and tensile strength relative to low density polyethylene (see OLEFIN POLYMERS). Toughness and flexibility are desired for film; high strength for piping. The relation of branching to crystallinity, molecular weight, and molecular weight distribution are important in achieving the desired properties in the product.

The principal use of LDPE and LLDPE in building products is as a film water barrier under below-grade floors; as a wall vapor barrier, though PVC is typically preferred; and as temporary enclosure film during construction. The film is made either by extruding a thin-walled tube, which may be slit or wound up directly, or by extrusion through a slot die and cast directly on to a cold roll, cooled, then wound up. The former method is more widely used. A much smaller use for low density polyethylene is in piping.

High Density Polyethylene. High density polyethylene (HDPE), 0.94–0.97 g cm^3, is a thermoplastic prepared commercially by two catalytic methods. In one, coordination catalysts are prepared from an aluminum alkyl and titanium tetrachloride in heptane. The other method uses metal oxide catalysts supported on a carrier (see CATALYSIS).

HDPE melts at about 135°C, is over 90% crystalline, and is quite linear, with more than 100 ethylene units per side chain. It is harder and more rigid than low density polyethylene and has a higher melting point, tensile strength, and heat-deflection temperature. The molecular weight distribution can be varied considerably with consequent changes in properties. Typically, polymers of high density polyethylene are more difficult to process than those of low density polyethylene.

Additives are used extensively in compounding this resin. Antioxidants (qv), uv stabilizers, especially carbon black (qv), and fillers (qv) such as glass fibers, silica, or clay provide properties desirable for various purposes.

High density polyethylene is widely used for pipes and drains, especially in large-diameter corrugated forms. The corrugations provide stronger walls at less thickness, which reduces the materials cost of the pipe.

Polypropylene. Polypropylene *[9003-07-0]* and high density polyethylene are both thermoplastics prepared with a coordination catalyst in the same type of equipment. The crystallinity of polypropylene gives it high tensile strength, stiffness, and hardness that are retained at high temperatures. It also is free from environmental stress-cracking. However, the hydrogen atoms bonded to tertiary carbons are susceptible to degradation by oxygen, uv light, and heat. Polypropylene, like high density polyethylene, can be stabilized by antioxidants and uv absorbers (see OLEFIN POLYMERS).

Polypropylene can be fabricated by almost any process used for plastics (see PLASTICS PROCESSING). The extrusion of pipe and injection molding of fittings present no unusual problem. However, there is no way to bond the fittings to the pipe except by remelting the polymer, which is impractical on most construction sites. The resin can be reinforced by glass fibers, mineral fillers, or other types of fillers and can be pigmented readily.

Poly(vinyl chloride). Poly(vinyl chloride) (PVC) *[9002-86-2]* is a thermoplastic for building products. It is prepared by either the bulk or the suspension polymerization process. In each process residual monomer is removed because it is carcinogenic. Oxygen must be avoided throughout the process (see VINYL POLYMERS).

The polymer is only slightly crystalline, mainly syndiotactic, but with so low a degree of order that only small crystallites are formed. It is fundamentally unstable to heat and light and loses hydrogen chloride by an autocatalytic reaction. Zinc and iron salts also strongly catalyze the decomposition. Many stabilizers, especially combinations of acid acceptors and antioxidants, produce satisfactory results except at high temperatures. The high density, a result of the high chlorine content, is offset by the low cost; thus the cost:volume ratio is quite attractive.

Vinyl chloride polymers are produced in two main types, homopolymers and copolymers, usually with vinyl acetate. Both types can be plasticized by a wide variety of plasticizers (qv), usually esters. Rigid or unplasticized PVC is used extensively for pipe. The plasticized material is used largely in floor coverings. The homopolymer itself is inherently fire-resistant, but addition of plasticizers, unless they are especially fire-resistant, considerably reduces this characteristic (see FLAME RETARDANTS).

Rigid, unplasticized PVC is stronger, with a higher tensile strength, than the polyolefins including polystyrene and ABS resins. It is not as strong as oxygenated polymers, eg, polyacrylics, polycarbonates, acetal resins (qv), and epoxy resins (qv), though it is similarly intermediate in elongation. Because of its instability to heat, rigid vinyl must be processed quickly, at low temperatures and correspondingly high pressures. PVC is the plastic used most widely in building products; nearly 60% of all PVC is used for this purpose.

Polystyrene. Polystyrene *[9003-53-6]* is a thermoplastic prepared by the polymerization of styrene, primarily the suspension or bulk processes. Polystyrene is a linear polymer that is atactic, amorphous, inert to acids and alkalies, but attacked by aromatic solvents and chlorinated hydrocarbons such as dry cleaning fluids. It is clear but yellows and crazes on outdoor exposure when attacked by uv light. It is brittle and does not accept plasticizers, though rubber can be compounded with it to raise the impact strength, ie, high impact polystyrene (HIPS). Its principal use in building products is as a foamed plastic (see FOAMED PLASTICS). The foams are used for interior trim, door and window frames, cabinetry, and, in the low density expanded form, for insulation (see STYRENE PLASTICS).

ABS Resins. Acrylonitrile–butadiene–styrene *[9003-56-9]* resins are thermoplastics that have a wide variety of composition, preparation conditions, and properties. Compositions generally run about 20–30% acrylonitrile, 20–30% butadiene, and 40–60% styrene. The resins are typically tough and rigid, easy to extrude or mold, and have good thermal and abrasion resistance. They can be alloyed and blended with other resins, especially poly(vinyl chloride) or polycarbonate *[24936-68-3]*, and can be shaped by almost any plastic-fabrication process: injection molding, extrusion, or thermoforming. They are used in automotive, marine, and communications applications. In building products, they are used for pipes, ducts, and structural foam. High impact grades used in piping have an Izod strength of over 400 J m (>7.5 ft lb in.) (see ACRYLONITRILE POLYMERS).

The structural foams are made by means of a blowing agent or by mixing a gas into the hot melt, then injecting it into a mold where the gas expands to form a cellular product. The foams are used for large parts in which light weight and rigidity are desired. Extrusion and free expansion are also used.

Polymethacrylates. Poly(methyl methacrylate) *[9011-14-7]* is a thermoplastic. It is the acrylic resin most used in building products, frequently as a blend or copolymer with other materials to improve its properties. The monomer is polymerized either by bulk or suspension processes. For glazing material, its greatest use, only the bulk process is used. Sheets are prepared either by casting between glass plates or by extrusion of pellets through a slit die. This second method is less expensive and more commonly used. Peroxide or azo initiators are used for the polymerization (see METHACRYLIC POLYMERS).

The polymer is clear and colorless and remains so on outdoor exposure; thus it often is used for glazing and lighting. Because the resin is softer than glass, various coatings are applied to improve its abrasion resistance. It is strong, tough and, when used as glazing, does not shatter if broken. These qualities render it suitable for vandal-resistant window panes and outdoor light globes. It also is used in plumbing fixtures, simulated-marble compositions, lavatory bowls, vanity tops, countertops, and bathtub–shower units.

Polycarbonates. Polycarbonates (qv) are partly crystalline thermoplastics with some disorder in the crystalline part and considerable order in the amorphous part. This disorder conveys high impact strength which, combined with its good transparency and outdoor exposure resistance, makes polycarbonates useful for vandal-resistant glazing and outdoor lighting. It is easily processed by extrusion and injection molding. Various uv and flame-retardant agents are often added.

Epoxy Resins. Epoxy resins (qv) or polyether resins are thermosets used as the binder for terrazzo flooring. The epoxy resin often is made from epichlorohydrin and bisphenol A. An excess of epichlorohydrin is used to assure that the intermediate product contains terminal epoxide groups. This resin, usually a viscous liquid, is mixed with fillers, pigments, and a curing agent. The mix is then applied to the substrate, and cure is obtained in a few hours. The product is strong, tough, and resistant to chemicals and abrasion. It is used for industrial and other floors subject to hard water. The use of epoxy resins for this purpose is only a small fraction of its total use.

Acetal Resins. Polyacetals are either homopolymer *[9002-81-7]* or copolymer *[95327-43-8]* thermoplastics (see ACETAL RESINS). Both are based on formaldehyde *[50-00-0]* through acetals or trioxane and are highly crystalline, strong, and rigid with high melting points. They are made in a variety of grades with different melt indexes and are processed easily by extrusion or injection molding. They can be reinforced with glass or fluorocarbon fibers and can be pigmented. Both have high resistance to creep and abrasion and low coefficients of friction. They are used as engineering resins and in building products for plumbing fittings such as ball cocks, faucets, pumps, and valves, which are subject to steady wear and must retain close dimensional tolerances. Polyacetals are flammable; however, because of the high oxygen content, they burn cleanly and produce no smoke (2–5).

Amino Resins. Amino resins (qv) include both urea- and melamine–formaldehyde condensation products. They are thermosets prepared similarly by the reaction of the amino groups in urea *[57-13-6]* or melamine *[108-78-1]* with formaldehyde to form the corresponding methylol derivatives, which are soluble in water or ethanol. To form plywood, particle board, and other wood products for adhesive or bonding purposes, a liquid resin is mixed with some acid catalyst and sprayed on the boards or granules, then cured and cross-linked under heat and pressure.

The decorative plastic laminates widely used for countertops and cabinets are based on melamine–formaldehyde resin (see LAMINATES). Several layers of phenolic-saturated kraft paper are placed in a press and a sheet of α-cellulose paper printed with the desired design and impregnated with melamine–formaldehyde resin is placed over them. Then a clear α-cellulose sheet, similarly impregnated with the resin, is placed on top to form a clear, protective surface over the decorative sheet. The assembly is cured under heat and pressure up to 138°C and 10 MPa (1450 psi). A similar process is used to make wall paneling, but because the surfaces need not be as resistant to abrasion and wear, laminates for wall panels are cured under lower pressure, about 2 MPa (290 psi).

Amino resins are lighter in color and have better tensile strength and hardness than phenolic resins; their impact strength and heat and water resistance are less than those of phenolics. The melamine–formaldehyde resins are harder and have better heat and moisture resistance than the urea resins, but they are also more expensive. The physical properties of the melamine–formaldehyde laminates are listed in Table 1.

Phenolic Resins. Phenolic resins *[9003-35-4]* (qv) are thermosets prepared by the reaction of phenol with formaldehyde, through either the base-catalyzed one-stage or the acid-catalyzed two-stage process. The liquid intermediate may be used as an adhesive and bonding resin for plywood, particle board, fiberboard, insulation, and cores for laminates. The physical properties for typical phenolic laminates made with wood are listed in Table 1.

Polyester Resins. Reinforced polyester resins are thermosets based on unsaturated polyesters from glycols and dibasic acids, either or both of which contain reactive double bonds. The ratio of saturated to unsaturated components controls the degree of cross-linking and thus the rigidity of the product (see POLYESTERS, UNSATURATED). Typically, the glycols and acids are esterified until a viscous liquid results, to which an inhibitor is added to prevent premature gelation. Addition of the monomer, usually styrene, reduces the viscosity to an easily workable level.

When the resin is to be used, fillers, eg, glass fibers, asbestos, or cotton, are mixed with it. The amount and kind of filler affect the strength, flexibility, and cost of the product. Alumina trihydrate acts as a fire-retardant when needed. Thixotropic agents control the viscosity and prevent the mix from draining from sloping surfaces. Pigments are used to provide color, usually white, and uv absorbers provide outdoor stability. To reduce smoke generation in burning resin and to improve outdoor stability, styrene can be replaced by methyl methacrylate. A peroxide catalyst and a combination of a cobalt soap and a tertiary amine are added as initiators (qv). The reaction is exothermic, and gelation is usually rapid.

For spas, shower stalls, bath tubs, etc, a gel coat containing no fiber reinforcement is applied first to the mold. It forms a smooth, strong, impervious, durable chemical, weather, and wear-resistant surface. The bulk of the resin, which may be reinforced with glass fiber, is applied by hand lay-up or by spray gun. The article is then cured at or near ambient conditions.

The physical properties of the reinforced polyester product made from chopped glass are listed in Table 1. The chemical resistance varies according to the composition but is generally good. Its principal uses in building products are for sanitary ware, eg, tub-shower units, and for panels, especially translucent or cement-filled types for roofing and walls of commercial or industrial buildings.

Polyurethane. Polyurethanes (pu) are predominantly thermosets. The preparation processes for polyurethane foams have several steps (see URETHANE POLYMERS) and many variations that lead to products of widely differing properties. Polyurethane foams can have quite low thermal conductivity values, among the lowest of all types of thermal insulation, and have replaced polystyrene and glass fiber as insulation in refrigeration. The sprayed-on foam can be applied to walls, roofs, tanks, and pipes, and between walls or surfacing materials directly. The slabs can be used as insulation in the usual ways.

Polylsocyanurates. Polyisocyanurates are thermosets prepared by condensation of 4,4′-methylenebis (phenyl isocyanate) *[101-68-8]* with an acidic, basic, or organometallic catalyst, or a combination of them, to form a six-membered ring (see CYANURIC AND ISOCYANURIC ACIDS). This structure is considerably more heat- and fire-resistant than urethanes, which dissociate at 100–130°C; the isocyanurates are stable to 350–500°C, probably because there is no hydrogen atom on the ring. Polyisocyanurate foams are rather brittle; therefore, they are modified with an active hydrogen compound to increase flexibility and resilience. The preparation of polyisocyanurate foams is similar to that of polyurethanes. Building panels for walls and roof decks are made by pouring the mixed components into a closed mold in which the liquid foams. A solid skin forms against the surface of the mold, which produces a skin integral with the matrix foam. The density of the foam decreases from surface to center.

Applications

The use of plastics in the U.S. building and construction sector increased at a rate of nearly 6% per year from 3,077,000 t in 1980 to 5,389,000 t in 1990 as shown in Table 2 (by resin class) and Table 3 (by market application). This advance is almost two times the overall U.S. GNP growth for the same period and is a testimony of plastics' increasing popularity as materials within the building and construction sector.

Table 2. Market Consumption by Polymer, 10^3 t[a]

Polymer	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	ACGR, %[b]
acrylics												
glazing and skylights	29.9	30.8	34.0	37.2	39.0	38.1	52.6	58.1	59.9	62.1	63.5	
lighting fixtures	9.1	10.0	13.2	15.0	15.0	15.0	14.5	17.7	20.0	21.3	20.4	
panels and siding	5.0	5.0	5.9	6.8	6.8	7.7	7.7	10.4	11.8	13.1	12.7	
plumbing	10.0	10.9	11.8	14.1	14.1	15.4	14.5	17.2	18.1	19.0	19.5	
Total	*54.0*	*56.7*	*64.9*	*73.0*	*74.8*	*76.2*	*89.4*	*103.4*	*109.8*	*115.6*	*116.1*	7.96
ABS												
pipe, fittings, conduit	110.2	99.8	59.9	79.8	82.1	56.7	70.3	74.8	69.9	70.3	63.5	5.37
acetal												
plumbing	8.2	9.1	9.1	10.9	11.8	13.2	5.9	6.4	6.8	4.5	2.3	11.90
butyrate												
panels and siding	1.8	1.8	1.8	1.8	1.8	1.8	1.8	2.3	2.3	2.3	2.3	2.40
cellulosics												
lighting fixtures	1.8	1.8	1.8	1.8	1.8	1.8	1.8	2.3	2.3	2.3	2.3	2.40
epoxy												
flooring[c]	8.2	8.2	6.8	8.2	6.8	8.2	7.7	9.5	11.3	11.3	11.8	
pipe, fittings conduit (coatings)	4.1	5.0	5.0	5.0	5.0	5.0	5.0	5.4	6.4	6.8	6.8	
Total	*12.2*	*13.2*	*11.8*	*13.2*	*11.8*	*13.2*	*12.7*	*15.0*	*17.7*	*18.1*	*18.6*	4.27
HDPE												
pipe, fittings, conduit	209.1	243.1	214.1	257.2	293.0	283.0	229.1	259.5	243.6	220.4	248.1	1.72

LDPE												
pipe, fittings, conduit	9.1	11.8	34.9	35.8	35.8	43.1	44.0	45.8	54.4	61.2	68.9	
vapor barriers	69.9	68.0	62.1	67.1	66.2	68.5	69.4	70.3	77.1	81.6	82.5	
Total	*78.9*	*79.8*	*97.1*	*103.0*	*102.1*	*111.6*	*113.4*	*116.1*	*131.5*	*142.9*	*151.4*	6.73
phenolic												
decorative laminates	20.0	15.0	14.1	16.8	16.8	14.5	18.1	21.8	31.3	40.3	31.7	
insulation	127.9	135.2	150.1	165.1	160.1	166.5	190.5	197.3	228.2	187.8	180.0	
resin-bonded woods	210.0	200.0	430.0	580.2	600.1	580.6	576.1	817.8	834.2	763.7	785.5	
Total	*357.9*	*350.2*	*594.2*	*762.1*	*777.0*	*761.6*	*784.7*	*1036.9*	*1093.7*	*991.8*	*997.2*	10.79
polycarbonate												
glazing and skylights	30.8	32.2	29.9	34.0	37.2	40.8	44.5	45.4	46.7	49.0	48.5	
lighting fixtures	4.1	4.1	3.2	4.1	4.1	4.1	4.5	4.5	5.0	5.4	5.4	
Total	*34.9*	*36.3*	*33.1*	*38.1*	*41.3*	*44.9*	*49.0*	*49.9*	*51.7*	*54.4*	*53.9*	4.43
polyester, reinforced[d]												
glazing and skylights	15.0	18.1	15.9	18.1	20.0	18.6	18.1	17.7	19.1	22.7	21.8	
panels and siding	64.9	69.9	59.9	79.8	84.8	55.3	55.8	52.2	53.1	56.7	54.4	
pipe, fittings, and conduit	99.8	104.8	94.8	110.2	117.9	61.7	62.1	63.0	64.9	71.7	68.0	
plumbing	59.9	64.9	59.0	72.1	74.8	45.8	46.3	45.4	50.8	52.1	51.2	
Total	*239.5*	*257.6*	*229.5*	*280.3*	*297.6*	*181.4*	*182.3*	*178.3*	*187.8*	*203.2*	*195.4*	2.01
polyester, thermoplastic (PBT)												
plumbing	3.2	1.8	3.2	3.2	5.0	2.7	3.2	3.2	3.2	3.1	3.2	0.00
polyethylene												
profile extrusion[e]	1.8	3.2	1.8	3.2	3.2	2.7	3.6	4.5	5.0	5.4	6.8	14.12
polypropylene												
pipe, fittings, and conduit	10.9	9.1	10.0	10.0	9.1	11.3	15.4	16.8	13.6	15.9	14.5	2.91
polystyrene												
insulation (foam)	79.8	81.2	87.1	93.0	108.9	79.4	75.3	78.5	108.0	109.8	105.2	
lighting fixtures	6.8	14.1	10.9	13.2	13.2	16.3	18.1	17.7	20.9	19.9	20.4	
pipe, fittings, and conduit	3.2	5.0	4.1	5.0	5.0	8.2	9.5	9.1	10.9	13.6	13.1	
plumbing	1.8	5.0	3.2	4.1	4.1	7.3	8.6	9.1	10.4	9.5	9.1	
profile extrusions	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	10.9	11.3	
wall coverings	4.1	9.1	6.8	8.2	8.2	9.5	10.0	11.3	12.2	12.2	12.7	
Total	*95.7*	*114.3*	*112.0*	*123.4*	*139.3*	*120.7*	*121.6*	*125.6*	*162.4*	*176.0*	*171.8*	6.02
polyurethane												
flooring (rug underlay-foam)[c]	49.9	52.2	44.9	54.9	54.9	53.5	59.0	61.2	145.2	145.1	158.7	
insulation (foam)	120.2	140.2	130.2	140.2	152.0	190.5	204.1	235.9	235.0	204.1	217.7	
Total	*170.1*	*192.3*	*175.1*	*195.0*	*206.8*	*244.0*	*263.1*	*297.1*	*380.1*	*349.2*	*376.4*	8.27
PVC												
flooring[c]	113.9	128.8	110.2	137.9	141.1	135.2	138.8	160.1	167.8	177.3	189.1	
lighting fixtures	6.8	8.2	6.8	8.2	9.1	8.2	13.6	15.9	16.3	13.6	13.1	
panels and siding	92.1	93.0	98.9	120.2	170.1	194.1	248.6	296.2	319.3	358.2	404.0	
pipe, fittings, and conduit	938.0	973.9	890.9	1106.8	1191.1	1376.7	1500.0	1580.8	1558.6	1439.9	1637.1	
profile extrusions[e]	53.1	52.2	73.0	92.1	112.0	128.8	139.7	160.1	149.7	152.3	159.1	
vapor barriers[f]	14.1	15.9	15.0	27.2	28.1	21.3	20.9	20.9	22.2	24.5	26.3	
wall coverings	22.2	20.0	16.8	19.1	19.1	16.3	17.2	29.9	31.3	31.3	35.3	
Total	*1240.1*	*1291.8*	*1211.6*	*1511.4*	*1670.6*	*1880.6*	*2078.8*	*2263.9*	*2265.3*	*2197.1*	*2464.0*	7.11
poly(phenylene oxide)												
plumbing	0.0	3.2	3.2	5.0	4.1	2.7	2.3	2.3	2.3	2.3	2.3	3.52
urea and melamine												
decorative laminates	11.8	15.9	10.9	16.8	20.0	20.0	20.4	23.6	18.6	30.8	18.1	
resin-bonded woods	435.0	463.1	346.1	435.0	459.0	446.3	458.1	511.7	512.6	439.9	481.1	
Total	*446.8*	*479.0*	*357.0*	*451.8*	*479.0*	*466.3*	*478.5*	*535.2*	*531.2*	*470.7*	*499.2*	1.12
Total	*3077.2*	*3244.1*	*3191.0*	*3924.1*	*4212.1*	*4276.5*	*4506.9*	*5093.4*	*5279.9*	*5045.5*	*5389.3*	5.76

[a] Ref. 6.

[b] Annual average compound growth rate (1980–1990).

[c] Excluding bonding or adhesive materials.

[d] Including reinforcements (1980–1984).

[e] Including windows, rainwater systems, etc.

[f] Including swimming pool liners.

Table 4 lists plastics consumed in building and construction vs total U.S. plastics consumption for 1990. There was more PVC consumed in the building and construction sector than any other resin type.

Table 3. Market Consumption by Application, 10^3 t[a]

Application	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990 Total	1990 Total,[b] %	ACGR,[c] %
decorative laminates													
phenolic	20.0	15.0	14.1	16.8	16.8	14.5	18.1	21.8	31.3	40.3	31.7		
urea and melamine	11.8	15.9	10.9	16.8	20.0	20.0	20.4	23.6	18.6	30.8	18.1		
Total	*31.8*	*30.8*	*24.9*	*33.6*	*36.7*	*34.5*	*38.6*	*45.4*	*49.9*	*71.1*	*49.8*	0.9	4.60
flooring[d]													
epoxy	8.2	8.2	6.8	8.2	6.8	8.2	7.7	9.5	11.3	11.3	11.8		
PVC	113.9	128.8	110.2	137.9	141.1	135.2	138.8	160.1	167.8	177.3	189.1		

urethane foam (rug underlay)	49.9	52.2	44.9	54.9	54.9	53.5	59.0	61.2	145.2	145.1	158.7		
Total	*171.9*	*189.1*	*161.9*	*200.9*	*202.8*	*196.9*	*205.5*	*230.9*	*324.3*	*333.7*	*359.6*	6.7	7.66
glazing and skylights													
acrylic	29.9	30.8	34.0	37.2	39.0	38.1	52.6	58.1	59.9	62.1	63.5		
reinforced polyester[e]	15.0	18.1	15.9	18.1	20.0	18.6	18.1	17.7	19.1	22.7	21.8		
polycarbonate	30.8	32.2	29.9	34.0	37.2	40.8	44.5	45.4	46.7	49.0	48.5		
Total	*75.8*	*81.2*	*79.8*	*89.4*	*96.2*	*97.5*	*115.2*	*121.1*	*125.6*	*133.8*	*133.8*	2.5	5.85
insulation													
phenolic (binder)	127.9	135.2	150.1	165.1	160.1	166.5	190.5	197.3	228.2	187.8	180.0		
polystyrene foam	79.8	81.2	87.1	93.0	108.9	79.4	75.3	78.5	108.0	109.8	105.2		
PU foam (rigid)	120.2	140.2	130.2	140.2	152.0	190.5	204.1	235.9	235.0	204.1	217.7		
Total	*328.0*	*356.5*	*367.4*	*398.3*	*420.9*	*436.4*	*469.9*	*511.7*	*571.1*	*501.7*	*502.9*	9.3	4.37
lighting fixtures													
acrylic	9.1	10.0	13.2	15.0	15.0	15.0	14.5	17.7	20.0	21.3	20.4		
cellulosics	1.8	1.8	1.8	1.8	1.8	1.8	1.8	2.3	2.3	2.3	2.3		
polycarbonate	4.1	4.1	3.2	4.1	4.1	4.1	4.5	4.5	5.0	5.4	5.4		
polystyrene	6.8	14.1	10.9	13.2	13.2	16.3	18.1	17.7	20.9	19.9	20.4		
PVC	6.8	8.2	6.8	8.2	9.1	8.2	13.6	15.9	16.3	13.6	13.1		
Total	*28.6*	*38.1*	*35.8*	*42.2*	*43.1*	*45.4*	*52.6*	*58.1*	*64.4*	*62.5*	*61.6*	1.1	7.98
panels and siding													
acrylic	5.0	5.0	5.9	6.8	6.8	7.7	7.7	10.4	11.8	13.1	12.7		
butyrate	1.8	1.8	1.8	1.8	1.8	1.8	1.8	2.3	2.3	2.3	2.3		
PVC	92.1	93.0	98.9	120.2	170.1	194.1	248.6	296.2	319.3	358.2	404.0		
reinforced polyester[e]	64.9	69.9	59.9	79.8	84.8	55.3	55.8	52.2	53.1	56.7	54.4		
Total	*163.7*	*169.6*	*166.5*	*208.7*	*263.5*	*259.0*	*313.9*	*361.1*	*386.5*	*430.3*	*473.4*	8.8	11.20
pipe, fittings, conduit													
ABS	110.2	99.8	59.9	79.8	82.1	56.7	70.3	74.8	69.9	70.3	63.5		
epoxy (coatings)	4.1	5.0	5.0	5.0	5.0	5.0	5.0	5.4	6.4	6.8	6.8		
HDPE	209.1	243.1	214.1	257.2	293.0	283.0	229.1	259.5	243.6	220.4	248.1		
LDPE	9.1	11.8	34.9	35.8	35.8	43.1	44.0	45.8	54.4	61.2	68.9		
polypropylene	10.9	9.1	10.0	10.0	9.1	11.3	15.4	16.8	13.6	15.9	14.5		
polystyrene	3.2	5.0	4.1	5.0	5.0	8.2	9.5	9.1	10.9	13.6	13.1		
PVC	938.0	973.9	890.9	1106.8	1191.1	1376.7	1500.0	1580.8	1558.6	1439.9	1637.1		
reinforced polyester[e]	99.8	104.8	94.8	110.2	117.9	61.7	62.1	63.0	64.9	71.7	68.0		
Total	*1384.4*	*1452.4*	*1313.6*	*1609.8*	*1739.1*	*1845.7*	*1935.5*	*2055.2*	*2022.1*	*1899.8*	*2120.0*	39.3	4.35
profile extrusions[f]													
PVC (including foam)	53.1	52.2	73.0	92.1	112.0	128.8	139.7	160.1	149.7	152.3	159.1		
polyethylene	1.8	3.2	1.8	3.2	3.2	2.7	3.6	4.5	5.0	5.4	6.8		
profile extrusions	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	10.9	11.3		
Total	*54.9*	*55.3*	*74.8*	*95.3*	*115.2*	*131.5*	*143.3*	*164.7*	*154.7*	*168.6*	*177.2*	3.3	12.43
plumbing													
acetal	8.2	9.1	9.1	10.9	11.8	13.2	5.9	6.4	6.8	4.5	2.3		
acrylic	10.0	10.9	11.8	14.1	14.1	15.4	14.5	17.2	18.1	19.0	19.5		
polyester, thermoplastic (PBT)	3.2	1.8	3.2	3.2	5.0	2.7	3.2	3.2	3.2	3.1	3.2		
PPO alloys	0.0	3.2	3.2	5.0	4.1	2.7	2.3	2.3	2.3	2.3	2.3		
polystyrene	1.8	5.0	3.2	4.1	4.1	7.3	8.6	9.1	10.4	9.5	9.1		
reinforced polyester[e]	59.9	64.9	59.0	72.1	74.8	45.8	46.3	45.4	50.8	52.1	51.2		
Total	*83.0*	*94.8*	*89.4*	*109.3*	*113.9*	*87.1*	*80.7*	*83.5*	*91.6*	*90.5*	*87.6*	1.6	0.54
bonded woods													
phenolic	210.0	200.0	430.0	580.2	600.1	580.6	576.1	817.8	834.2	763.7	785.5		
urea and melamine	435.0	463.1	346.1	435.0	459.0	446.3	458.1	511.7	512.6	439.9	481.1		
Total	*645.0*	*663.2*	*776.1*	*1015.2*	*1059.1*	*1026.9*	*1034.2*	*1329.5*	*1346.7*	*1203.6*	*1266.6*	23.5	6.98
vapor-barriers													
LDPE	69.9	68.0	62.1	67.1	66.2	68.5	69.4	70.3	77.1	81.6	82.5		
PVC[g]	14.1	15.9	15.0	27.2	28.1	21.3	20.9	20.9	22.2	24.5	26.3		
Total	*83.9*	*83.9*	*77.1*	*94.3*	*94.3*	*89.8*	*90.3*	*91.2*	*99.3*	*106.1*	*108.8*	2.0	2.63
wall coverings													
polystyrene	4.1	9.1	6.8	8.2	8.2	9.5	10.0	11.3	12.2	12.2	12.7		
PVC	22.2	20.0	16.8	19.1	19.1	16.3	17.2	29.9	31.3	31.3	35.3		
Total	*26.3*	*29.0*	*23.6*	*27.2*	*27.2*	*25.9*	*27.2*	*41.3*	*43.5*	*43.5*	*48.0*	0.9	6.20
Total	*3077.2*	*3244.1*	*3191.1*	*3924.1*	*4212.1*	*4276.5*	*4506.9*	*5093.4*	*5279.9*	*5045.5*	*5389.3*	100	5.76

[a] Ref. 6.

[b] Total 1990 plastics consumption, %.

[c] Annual average compound growth rate (1980–1990).

[d] Excluding bonding or adhesive materials.

[e] Including reinforcements (1980–1984).

[f] Including windows, rainwater systems, etc.

[g] Including swimming pool liners.

Table 4. Sales Volume of Selected Polymers, 1990, 10^3 t[a]

Resin	Total U.S. consumption	Use in building and construction	Total consumption, %

PVC	4216.3	2464.0	58%
phenolic	1282.0	997.2	78%
urea and melamine	652.6	499.2	76%
polyurethane	1480.7	376.4	25%
HDPE	3857.1	248.1	6%
polyester, reinforced	721.0	195.4	27%
polystyrene	2329.7	171.8	7%
LLDPE LDPE	5385.9	151.4	3%
acrylic	340.5	116.1	34%
ABS	549.7	63.5	12%
polycarbonate	281.2	53.9	19%
epoxy	210.4	18.6	9%
polypropylene	3688.0	14.5	0.4%
other polyethylene	na	6.8	na
polyester, thermoplastic[b]	89.8	3.2	4%
acetal	65.0	2.3	4%
cellulosics	36.3	2.3	6%
butyrate	14.0	2.3	16%
mPPO[c] alloys	90.2	2.3	3%
Total	*25290.4*	*5389.3*	*21%*

[a] Ref. 7.

[b] Poly(butylene terephthalate) (PBT) *[24968-12-5]* and others.

[c] Modified poly(phenylene oxide).

Phenolics are consumed at roughly half the volume of PVC, and all other plastics are consumed in low volume quantities, mostly in single application niches, unlike workhorse resins such as PVC, phenolic, urea–melamine, and polyurethane. More expensive engineering resins have a very limited role in the building materials sector except where specific value-added properties for a premium are justified. Except for the potential role of recycled engineering plastics in certain applications, the competitive nature of this market and the emphasis placed on end use economics indicates that commodity plastics will continue to dominate in consumption. The application content of each resin type is noted in Table 2. Comparative prices can be seen in Table 5. The most dynamic growth among important sector resins has been seen with phenolic, acrylic, polyurethane, LLDPE LDPE, PVC, and polystyrene.

Table 5. Prices of Plastics Used for Building and Construction, $/kg[a]

Plastic	1983	1985	1987	1989
ABS, medium impact	1.90	1.94	1.63	1.98
acrylic, impact	2.23	2.23	2.03	2.38
cellulose acetate	2.84	2.84	2.84	2.84
epoxy, general purpose	2.53	2.56	2.56	2.56
phenolic	1.01	1.01	0.95	1.22
polyacetal, copolymer	3.26	3.44	3.44	2.76
polycarbonate, extrusion-grade	3.55	3.73	3.59	3.20
unsaturated polyester, general purpose	1.10	1.04	1.43	1.37
HDPE, pipe-grade	0.95	0.82	0.95	1.19
LDPE, liner-grade	0.88	0.79	0.82	0.90
PP, general purpose homo, extrusion-grade	0.84	0.77	1.01	0.90
PS, general purpose crystal-grade	0.86	0.71	1.21	1.17
PS, expandable beads	1.41	1.23	1.46	1.57
PU—polymeric MDI	1.79	1.61	1.61	1.72
PU—80 20% TDI	1.98	1.61	2.09	2.09
PVC, pipe-grade	0.71	0.57	0.84	0.77
melamine	1.52	1.54	1.54	1.61
urea–formaldehyde	1.08	1.10	1.10	1.10
PBT, glass-filled	3.53	3.75	3.46	3.31
nylon-6, unfilled	3.51	3.51	3.02	2.69
nylon-6,6, unfilled	3.99	4.28	3.90	3.02
mPPO, extrusion-grade	2.89	2.89	3.09	3.31

[a] Ref. 8.

Over 60% of the total plastics volume for building materials is consumed for pipes, fittings, conduit, and wood bonding applications. Other important applications include insulation, panels and siding, and flooring (additional 25%). Ten-year growth has been greatest in profile extrusions, panels and siding, flooring, lighting fixtures, and wood bonding applications. Table 3 provides the percentage of total 1990 plastics consumption for each application (9–11).

Solar Heating. Plastics are used in both active and passive solar-heating systems. They are used more frequently in passive systems because of their lower operating temperature, but many components of active systems are also made of plastics. Components under development include carbon-filled polypropylene pipes and poly(phenylene oxide) (PPO) plates and pipes. As covers, polycarbonate, polyacrylate, cellulose acetate–butyrate, and glass-fiber-reinforced polyester all transmit solar heat well and are resistant to uv light. Additional protection from uv radiation is provided by films of poly(vinyl fluoride), acrylate, or a new fluorocarbon film that is stable to sunlight. For frames to hold the assembly, high density polyethylene, ABS, polycarbonate, or rigid structural polyurethane foam can be used. Insulation behind the absorber plates can be of foamed plastic, especially foamed polyisocyanurate, which has good heat resistance. Phenolic-bonded glass fiber may vaporize and fog the inside of the cover but is necessary for high temperature use. Polyurethane foam also can be used. Several designs for single-piece solar collectors that incorporate a collector consisting of carbon black-loaded, cross-linkable polyethylene have also been introduced.

Focusing collectors are usually cast acrylic Fresnel lenses, or mirrors of aluminized polyester film in frames of aluminum. These reflectors are either enclosed in a bubble of poly(vinyl fluoride) film, or under polycarbonate glazing, which may be covered with a fluorocarbon film to reduce the reflectivity. The absorbers for active systems are copper or aluminum since the temperatures are too high (325–370°C) for plastics. The frames, however, can be molded ABS, high density polyethylene or polyurethane, either solid or structural foam. Polybutylene or chlorinated PVC can be used for piping hot water, and tanks can be made of either reinforced polyester or blow- or rotational-molded, high density polyethylene (12–15).

Thermal Insulation. Foamed plastics (qv) are used as thermal insulation for all types of construction because of their low heat- and moisture-transmission values. Polystyrene is used either as foamed board or expandable beads. The foam may be faced with a structural surfacing material, eg, a kraft liner-board, to form a panel for insulating mobile homes. These foams can duplicate the appearance of wood and be used as trim. Foams can also be used as backing, for example, on aluminum siding, to provide heat and sound insulation. Foamed beads can be incorporated in concrete to reduce its density and provide some thermal insulation.

Poly(vinyl chloride) foams may be rigid or flexible; the rigid foams are used to replace wood for interior trim and some door frames where the insulating properties are advantageous. They are dry-blended with a chemical blowing agent, fed to an extruder at 180–200°C, and passed through a profile die, which provides up to 8 cm of land length. The die temperature should be cooler than the stock temperature to produce a good surface. The melt expands upon leaving the die; then it is sized and cooled.

Polyurethane foams for building purposes are normally of the rigid kind used for roof and wall insulation. Polyols containing halogen or phosphorus are used to increase the fire resistance of the foam.

Polyisocyanurate foams are superior to others in fire-resistance. The initial step in their preparation is the trimerization of MDI to form a ring quite stable to heat. This polymer is mixed with blowing agents, as for polyurethanes, and expanded to obtain a low density closed-cell foam, stable up to 150°C. The process may be used for continuous buns or laminates. The product has dimensional stability and is much more fire-resistant than polyurethane foams. In some fabrication, the foam is poured at a rate of 4.5–9.0 kg min between facings held vertically in a jig and then allowed to expand. The board can be removed from the jig after about one minute per 2.5 cm of board thickness. Because the pressure developed is not more than 0.14 MPa (20 psi), lightly built jigs can be used. The facings may differ in shape and material. Boards of 2.5–23 cm thickness and from 1.2 × 2.4 m to 4.5 × 12 m have been made. The foam has uniform density from bottom to top and from side to side. It is used in wall and ceiling systems with a great variety of assembly and installation procedures. The wide choice of thickness, facing material, and foam density renders it suitable for many different construction designs. It is somewhat more expensive than polyurethane foam products.

The need to conserve energy and keep heat inside homes (insulate) is a driving force behind the growing use of insulative materials. U.S. homes have made drastic improvements in energy efficiency since the first energy shocks of the early 1970s. Between 1972 and 1986 energy use per household fell 34%. Thermal insulation products compete on a cost performance basis, where performance includes such factors as thickness, density, and thermal insulation rating (*R*-value). Several plastic foams compete for the thermal insulation market in the U.S. building and construction industry. They include polyisocyanurate boardstocks, sprayed-up polyurethane foams, extruded polystyrene board, board made from molded blocks of expandable polystyrene (EPS), and phenolic foam. Although other foams exist, they are either too expensive or lack the insulative properties required to be competitive. Table 6 compares the thickness (cm) of insulation required to achieve the *R*-values shown.

Table 6. *R*-Values vs Insulation Thickness for Selected Plastics[a]

Insulation material	*K*-Factor[c]	*R*-Value[b] for thickness in cm				Relative cost[d]
		7	5.3	3.5	1.8	
phenolic, aged	1.73	12.2	9.1	6.1	3.0	4
polyurethane or polyisocyanurate, aged	2.60	18.3	13.7	9.1	4.6	3
extruded polystyrene	2.88	20.3	15.2	10.2	5.1	2
expanded polystyrene	3.46	24.4	18.3	12.2	6.1	1
glass fiber	4.03	28.4	21.3	14.2	7.1	
foamed glass	5.04	35.6	26.7	17.8	8.9	
mineral wool	5.04	35.6	26.7	17.8	8.9	
perlite	5.62	39.6	29.7	19.8	9.9	
vermiculite	6.91	48.8	36.6	24.4	12.2	

[a] Ref. 16.

[b] *R*-Values are directly proportional to thickness shown. To convert *R*-value in $m^2 \cdot K$ W to $h \cdot ft^2 \cdot °F$ Btu, multiply by 5.7.

[c] *K*-Factor data for phenolic supplied by Manville; source for all other *K*-factors is The Dow Chemical Company. Units of *K*-factor are (W·cm) $hm^2 \cdot K$ (1.4 Btu·in. h·sq ft·°F). *R*-Value per cm of thickness is the *K*-factor. *K*- and *R*-factors can vary with age and use conditions. Values shown are averages obtained from lab samples.

[d] 1 best; 4 worst.

Based on performance (thermal insulation), polyisocyanurate, polyurethane, and phenolic foams have the lowest thermal conductivities, mainly because of the blowing agent used in their respective processes (CFC-11). Preventing the loss of CFC (chlorofluorocarbon) through such techniques as adding impermeable skins, eg, metal foils, is critical to maintaining the long-term insulation value of such foams as polyisocyanurate and polyurethane but also raises the cost. Although the relative cost of expanded polystyrene is the lowest among the key plastic foams and phenolic is the highest, sheet thickness, building codes, temperature resistance (both environmental and via the application of roofing tars), and the overriding concern of long-term insulation performance, help determine the actual choice of materials. All candidates have their place in various building and construction applications, eg, roofing and wall insulation.

Environmental considerations have dramatically affected the future prognosis of thermal insulation materials based on their heavy reliance on chemical blowing agents such as CFC-11 and pentane for insulation performance. CFC-11, along with other fully halogenated chlorofluorocarbons, has been linked with ozone depletion and the potential of global warming. Pentane has been linked to environmental pressure to reduce volatile organic emissions (VOC), also believed to contribute to ozone depletion. Under the Montreal Protocol, the primary industrial nations of the world have agreed to control the use and production of CFCs. The protocol requires signatory nations to reduce 1986 CFC consumption by 20% in 1993, and 50% in 1998. Because of the distribution of CFC use in the United States, the primary impact to the plastics industry of the Montreal Protocol will be felt in the rigid foam (insulation) segment, where CFC use has significantly contributed to product performance. Developmental efforts aimed at phasing out CFC consumption have centered on such alternatives as hydrochlorofluorocarbons (HCFCs), eg, HCFC-123, HCFC-1416, hydrofluorocarbons (HFCs), and use of blends including HCFCs or HFCs plus carbon dioxide generated by the addition of water, which reacts with isocyanates. Unfortunately, toxicity and ozone-depletion concerns remain for the proposed alternatives and these alternatives only approximate the performance standards set down by the original CFC-based formula. The concern to the polymer plastics fabricating industries, despite huge current and continuing investments in new technologies, is the threat that thermal insulation products could move to nonplastic forms of insulation (12,13,17–31).

Roofing. Roofing membranes are used on residential and nonresidential buildings. In 1989, nonresidential buildings represented 70% of the roofing market dollar volume. Within each segment, reroofing represents greater than 70% of the activity compared to new constructions. In general, residential roofing systems do not employ polymers; they use materials such as asphalt shingles, concrete, clay tiles, and treated wood. Nonresidential roofing systems include single-ply, built-up, modified bitumen, and metal. Polymeric materials used in the single-ply segment of nonresidential roofing systems include PVC and PVC alloys, chlorosulfonated polyethylene (CSPE), chlorinated polyethylene (CPE), and ethylene–propylene diene rubber (EPDM). Built-up roofs dominate (32% for 1989) among nonresidential material systems.

Among other polymers used in this market, EPDM (30%) leads followed by PVC PVC alloys (5%), and CSPE CPE (3%). Modified bitumen (20%) and metal (10%) have the remainder of the market. Single-ply material systems including PVC PVC alloys, EPDM, and CSPE CPE are gaining share, with PVC expected to grow at about 5–6% yr over the next five years.

PVC PVC alloys have advantages in seaming (heat seaming and radio frequency welding), flexibility, repairability, permeability, and winter installation; disadvantages include cost, reputation for prior failures, cold-cracking related to plasticizer migration, and incompatibility with asphalt coal-tar. CSPE CPE have advantages in chemical resistance, compatibility with asphalt coal-tar, ability to withstand high temperatures, and durability; disadvantages include cost, curing after exposure, repairability, susceptibility to algae, and chalking thinning. Being an elastomer, EPDM has advantages in cost and elongation; disadvantages include seaming and emissions from solvent-based adhesives. Modified bitumen has advantages in seaming with torching, compatibility with asphalt coal-tar, repairability, and similarity to built-up roofing (labor advantage); disadvantages include durability, safety component relating to the torching operation, seaming with mopped-on asphalt, and narrow widths. Built-up roofs have the simple advantage of low cost and the disadvantage of poor durability.

Development efforts in alloying offer PVC and PVC alloys the opportunity to capture shares from the higher performing chlorinated and chlorosulfonated polyethylenes (CPE CSPE). Alloys including PVC copolymer, nitrile–butadiene rubber, ethylene interpolymer, and tripolymers already have an estimated 35% of the PVC PVC alloy segment with plasticized PVC homopolymer controlling the remaining 65%. Developmental thrusts to date have included the incorporation of elastomeric modifiers in vinyl systems so low temperature flexibility could be attained without total reliance on plasticizers. In the early 1980s PVC roof membranes that relied entirely on plasticizers for flexibility failed when environmental conditions, including contact with the ballast, caused the plasticizers to migrate and leach out of the membrane, and the resulting unreinforced membrane experienced cold-cracking, embrittlement, and loss of properties. Additional development centered around the use of higher molecular weight plasticizer less susceptible to migration. Developments of this type have allowed PVC to restore its reputation and stage a comeback in this market.

Calendered PVC has approximately 55% of the PVC PVC alloy segment, PVC dispersion coatings using a reinforcement are 40%, and PVC extrusion with width limitations is about 5%. Almost all PVC membranes are reinforced or supported with thicknesses from 1.2–2.4 mm (47–96) mils. Converters typically purchase rollstock in 5–6 ft widths (1.5–1.8 m). Colors and designs are not common; most manufacturers offer a solid white, gray, or tan sheet.

Important trends in this market include a shortage of labor because of regulations on worker exposure, growth of single-ply roofing that are easier to install and need less equipment, growth of reroofing (stagnant new growth, short lives of traditional materials, spill-over of past failures), lower prices (pressure from EPDM), use of reinforced and thicker sheets (memory of failures), and increasing performance targets (alloy development) (12,13,30,32–38).

Swimming Pools and Spas. Swimming pools in the United States are both in-ground and above-ground types for residential, commercial, and institutional markets. There is a need for a vapor barrier in the construction of pools for which calendered (flexible) PVC is the primary material used. By their nature, above-ground pools are concrete (63%), fiberglass (3%), or vinyl-lined (34%). A replacement pool market parallels the types of pools mentioned above. Above-ground pools consume about 54% of the PVC used as pool liners, and in-ground types consume the rest. The replacement market is beginning to dominate the consumption of PVC for both types of pools based on the already high and escalating cost of new pools. Vinyl-lined pools are maintained easily, typically cost less than prepackaged alternatives, and are available in a variety of designs. Their disadvantages include limited flexibility in design shape and the perception that they are cheap. Fiber glass, typically reinforced polyester, is characterized by longer life and ease of cleaning but suffers from limited sizes shapes, limited colors, availability only near manufacturing sites, and sensitivity to improperly maintained poolwater chemistry. Concrete pools offer design flexibility, more permanent stronger perception, and status orientation but are more costly than alternatives, require more chemicals, and are more difficult to clean.

In-ground pool liners are typically calendered flexible PVC, 0.5 mm (20 mil) in thickness, that are printed. Above-ground liners are typically calendered flexible PVC, 0.3–0.5 mm in thickness, with some printing and embossing. About 80% of the PVC in this market is calendered with consistent thickness across the roll and high print quality; the rest is extruded. The PVC formulation used in this market has the advantage of uv stability, cold-crack resistance, resistance to algae, low shrinkage, low cost, and flexibility. Decorative aspects including color and exclusive prints are outstanding. Growth for PVC in pool liners is estimated at 3–4% yr in the early 1990s, with the replacement markets gaining dominance.

Historically, spas and hot tubs were compression molded thermoset composite systems, including reinforced unsaturated polyesters. Since the early 1980s, thermoformed thermoplastic, generally a coextruded sheet of weatherable polymer like acrylonitrile–styrene–acrylate (ASA) on a substrate of ABS, has taken this market from thermoset composites. The thermosets were found to be vulnerable to attack by algae. By employing ASA as an outer surface, the weatherability and chemical resistance to cleaning compounds of the thermoplastics is greatly improved. New low profile surface systems under development include resin mixtures with unsaturated polyester, including dicyclopentadiene, that offer pigmented appearance and aesthetics that rival natural marble. Performance attributes in this area include class A appearance, which is a high quality finish, structural integrity including uniform properties, reasonable cost, acceptable processability, improved fire and smoke resistance, and low VOC emissions.

Important trends in this market include the 30% decrease of the new pool market over the past two years (1989–1990), and the trend toward printed above-ground liners with unique designs (39).

Electrical Applications. Plastics are used for electrical insulation, conduit and enclosures, lighting fixtures, and mechanical devices. The most widely used plastic for wire and cable insulation is flexible, plasticized PVC, which constitutes well over half the market in insulating wires for buildings, automobiles, appliances, and power and control lines. Polyethylene is also a factor. Higher performance plastics such as nylon and fluoropolymers also play a smaller role in this area.

Electrical conduit includes several metals that account for roughly 65% of the market and PVC, which accounts for the remaining 35%. Conduit is used primarily to protect electrical wiring from mechanical and environmental damage. PVC is nonconductive, nonsparking, and inherently fire-resistant. In addition, it does not corrode, has high impact resistance, and its smooth uniform interior walls make wire pull-through easier, faster, and less prone to damage. Driven by its commanding cost advantage over competing metals (25–55%), it is anticipated that PVCs share of the general conduit market will continue to grow into the 1990s. In control and communication wire there is a trend away from traditional vinyl or other polyolefin-based insulation. Significant savings can be realized by using plenum-rated perfluorinated resin-jacketed wire, which may be run or rerun as needed in drop ceilings or raised floors without conduit.

For switch and motor housings, engineering resins such as thermoplastic poly(phenylene oxide) that has high impact strength, allowing thin walls, is used. With its low moisture absorption, it is a good electric insulator. It is also corrosion-, heat-, and fire-resistant. Polycarbonate is used for switches and outdoor electrical plugs because of its good low temperature impact strength and fire resistance. For lighting fixtures, polycarbonate is useful not only as a sheet glazing material for electrical lighting, based on its transparency, but also for molding housings and outdoor fixtures. Thermoplastic polyesters, eg, PBT, PET, and PCT (poly(cyclohexane-1,4-dimethanol terephthalate)), are playing increasingly important roles in such electrical applications as switches, wiring devices, connectors, and relays. Reinforced polyesters (thermoset) also play a role in power boxes based on their composite structural integrity and dimensional stability. Epoxies play an important role in electrical laminates, eg, printed circuit boards, whereas high heat thermoplastics, eg, polyetherimide (PEI), polyethersulfone (PES), and polysulfone (PSO), are now penetrating this market via injection molding technologies. Overall, the superior performance of engineering thermoplastics will allow them to continue to grow in electronic applications as spaces become more confined and heat requirements increase. However, for the foreseeable future, workhorse resins such as PVC, LDPE, HDPE, ABS, and phenolic will continue to dominate (12,40–42).

Glazing. Polyacrylates and polycarbonates are the resins most widely used for glazing. They are light in weight, easily formed, and provide heat and sound insulation. Their chief advantage is their resistance to breakage and their failure to shatter when they break. Coatings of fluoropolymers often are used to improve abrasion resistance, and cross-linked polysilicate, almost as hard as glass, has been used. Some grades of polyacrylates can be cemented with solvents instead of with adhesives that need curing. The surface can be rippled or given a matte finish, or it can act as a sunscreen.

Polycarbonates are dimensionally more stable, have high impact strength and heat resistance, provide thermal insulation, and are fire-resistant. Surface coatings of more abrasion-resistant films can be applied. Polyacrylates have been introduced for glazing where the amber tint and high temperature resistance, over 150°C, are advantageous. Their present cost limits their use to extreme service conditions. Architectural-grade fiber glass reinforced plastic (FRP) can also be used in translucent panel skylight systems. Panel widths of up to five feet (1.5 m) are manufactured as a sandwich consisting of FRP bonded under controlled heat and pressure to a mechanically interlocked aluminum I-beam grid core.

Plastic conductive (metallized) films are also used in conjunction with glass surfaces to create an active window system capable of achieving over 90% the insulating performance of a solid wall. The metallized film surface allows visible light transmission while blocking heat and uv light radiation. Security safety windows are manufactured by laminating an inner layer film of poly(vinyl butyral) between an inner and outer layer of tempered glass. This construction is frequently used in high security applications such as jewelry store display windows or prisons and is similar to automotive safety glass.

Windows comprise a relatively small amount of the total exterior surface area of a house; however, it is estimated that they account for nearly 25% of a home's total energy costs via thermal losses such as conduction, convection, and radiation. In 1991, California was debating a proposed system for window energy performance ratings based on their high importance as a source of heat loss. This rating, if enacted as legislation, is part of a proposed comprehensive energy code that California is considering. It would require window manufacturers to display the thermal conduction ratings (*R*-values) of their products. Single-pane glass has a relatively low *R*-value of about *R*-1. Double-pane windows rate about *R*-2. The active window systems described above are capable of values as high as *R*-4 to *R*-8 (12,13,31,34,43–47).

Siding. The resin most used for siding is poly(vinyl chloride) homopolymer, compounded with modifiers, stabilizers, and pigments. Modifiers are most often acrylic esters, followed by chlorinated polyethylene or ethylene–vinyl acetate, used at 6–8 phr (parts per hundred resin). The modifier increases the impact strength of the rigid PVC.

Heat stabilizers are usually methyl- or butyltin compounds at 1.5–2.5 phr. New alternatives to organotins include mixed metal stabilizers such as barium–zinc or calcium–zinc. Other organotin and barium–cadmium stabilizers are being developed that would permit the use of less TiO_2 in the composition. In light colors TiO_2 is a pigment, but it also functions as a uv screen. If less TiO_2 is used, stabilization must be increased by other means. A barium–cadmium phosphite with an epoxy-plasticizer stabilizing system is said to be so effective that TiO_2 can be eliminated. However, the liquid components reduce the heat distortion temperature and impact strength so that more rigid modifiers may be needed. In further efforts to reduce costs, compounding is done by the extruder, thereby eliminating the pelletizing step by high intensity dry-blend mixing of powders that are fed directly to the extruders. This method also reduces the heat exposure and provides better quality with reduced amounts of stabilizers.

Siding is usually produced by extrusion of the PVC composition through a profile die. It also is prepared by extruding a flat sheet, embossing it, then postforming it in a press. This process is relatively low cost at a high production rate, up to 270 kg h, but the appearance obtained with extruded profiles is usually preferred. Extruded profiles are conventionally cooled with air, which requires a cooling length of 7.5–10.5 m. In some new processes the profile is held by means of a vacuum against a metal shape, through which water at a controlled temperature is passed. The profile is thus cooled at a controlled rate, in a shorter time, and with less residual internal stress. The profile cooled in this manner shows about 1.5% shrinkage after 30 minutes at 30°C, as compared with 2–5% by conventional cooling. Output rates are 135–160 kg h. The product also has a higher impact strength. In another process more tolerant of formulation changes, some producers use twin-screw extruders to get high shear, lower temperatures with less power, and little or no backflow. The design of the dies and the control of stresses during cooling are vitally important to obtain a good product.

Another technology trend is the growing use of coextrusion for the production of vinyl siding. Dual, coupled extruders are used in conjunction with a multislot die to allow a two-layer profile to be extruded. The lower, or substrate, layer provides mechanical rigidity but, because it does not face exposure to the environment directly, it can be manufactured using less expensive grades of PVC along with lower levels of expensive additives such as heat and uv stabilizers plus colorants. The top, or capstock, layer of the profile that comprises the surface of the siding is compounded with the higher levels of additives required for color stability, weatherability, eg, resistance to chalking, etc. Careful compounding is necessary to obtain adequate physical properties including controlled cooling to avoid dimensional changes that lead to oil-canning, which is the uneven stress-relaxation and thermal expansion that cause distortion.

The postextrusion phase of the process is usually the most difficult to accelerate and is the controlling limit on line speed, which often is no more than 4.5–9.0 m min. The numerous stages include an embosser, vacuum-sizing calibration, cooling, pulling, punching, cutting, and stacking.

Residual stress in PVC is a factor in heat distortion of siding. When the sun shines on an installed strip of siding, the center of the strip becomes hotter than the edges or the covered portion. The various temperatures have been measured and resulting stresses estimated; to counteract these stresses, residual stresses have been set up in certain areas of the strip during production. Quenching the shaded portion, the butt, and the hanger creates compressive stresses; tensile stresses are produced by cooling the center slowly. When the siding is exposed to hot sunlight, the center shrinks and the shaded portions expand, thereby counteracting the oil-canning caused by thermal expansion. Thus, a good appearance is maintained.

Although PVC has several advantages as a siding and affords good impact resistance and low sound transmission, only in light colors does it offer adequate resistance to outdoor heat and light. Manufacturers who wish to produce PVC siding in dark or earth colors have had to consider the high cost of pigments and the fact that the TiO_2 used in light colors acts both as a pigment and stabilizer. If the TiO_2 is eliminated, more stabilizer must be used; if it is retained, more pigment must be used. One way to overcome this problem is to use coextrusion of a dark colored, thin-walled capstock over a low cost, less pigmented substrate or core. Another process uses a foamed rather than a solid core, and the coextruded film provides a smooth, dark colored skin. The components may also be resins other than PVC. Acrylic films, which are inherently light-stable, have been coextruded over PVC or chlorinated PVC substrates. Both methods raise the cost.

The usual inorganic pigments for dark colors may contain iron or other metal ions that can adversely affect the stability of PVC. Some organic pigments, though more expensive, contain only traces of heavy metals. Because inorganic pigments reflect more ir radiation, less heat is absorbed by the plastic, whereas organic pigments have a high tinting strength and hiding power over TiO_2. Pricing according to color may be necessary. The inherent fire resistance of rigid PVC and its high flash-ignition temperature are definite advantages for its use in construction. However, once burning, PVC can generate toxic gases such as hydrochloric acid, HCl.

Another PVC siding is an extruded product of an internally ribbed, dual-wall profile. A conventional screw extruder, with a vacuum sizer cooled with water and air, forms a product about 20 cm wide with 160 mm walls and 80 mm ribs on 25 cm centers. The total thickness is about 0.64 cm. The ribs provide rigidity and strength and the dual-wall construction adds thermal insulation. No backing or core is used.

A recently introduced polycarbonate-based blend offers a low coefficient of thermal expansion. This new thermoplastic is designed for large sheet applications such as doors or siding. Its high dimensional stability will eliminate warping from exposure to varying temperatures.

Outdoor building products such as guttering, siding, and roofing have seen sharp increases with the recent remodeling boom. Vinyl siding will continue to grow at nearly 5% per year at the expense of brick and aluminum siding and as a substitute for painting. Residential use will comprise 90% of the total market with the do-it-yourself market becoming more important. Vinyl siding accounted for 80% of all siding replacement work in the late 1980s but was used on less than 10% of new single-family homes in the same year. Vinyl siding is growing in popularity because of increased consumer acceptance, its attractive appearance, and low maintenance features. A 30% share of the new home market is anticipated for vinyl siding by 1995 (11,12,33,34,48–59).

Shutters and Exterior Trim. These have been made largely from thermoformed rigid cellular PVC. Foaming the PVC and reducing its density from 1.4 to 0.4–0.5 g cm^3 reduces the cost considerably though the composition itself is somewhat more expensive. Thermoforming may produce either cut-sheet or roll-sheet. The former uses stock up to 1.25 cm thick, the latter is limited to no more than 0.625 cm thickness. An extruder line may feed directly to a roll-sheet thermoformer line. Metal or wood reinforcements may be provided for structural support. Shutter and other exterior trim can also be extruded by conventional single-screw machines. Dies may be designed to allow the extrudate to expand to give a balanced flow to the sizing die, which holds and cools the extrudate to the desired dimensions, and allows for some residual shrinkage during final cooling. For large profiles from PVC foam, the Celuka process can be used, whereby the hot and sizing dies are the same size, which causes an inward expansion in the hollow core. This product has a thicker skin and a more variable cell structure than normal extrudate. All the problems and solutions that apply to siding, including capstock coextrusion for dark colors, apply to these products as well. Shutters have also been made from high impact polystyrene foam coated with an acrylic ester and from ABS capped with acrylic ester to provide protection from uv light and improve outdoor weatherability (32,33,40,58,60).

Door and Window Frames and Sashes. The first successful application of rigid PVC for windows was as a cladding over a wood core to avoid the need for painting and repainting the sash and the exterior of the frame. Since then, extruded profiles of rigid PVC have been developed to allow

door and window frames and sashes that do not rot, corrode, or need paint and that provide good insulation and low air infiltration. One window system extrudes profiles 1.8-mm thick with a series of closed channels for rigidity, thermal insulation, and low cost. The extrudate is cooled with a vacuum calibrator, then cooled further by forced air, sawn, cut, and the corners mitered. The pieces are put in holding jigs and holes are drilled for screws. Corners are secured with metal braces to resist the spring-loaded sash weight and to hold the screws. Joints are sealed with silicone polymers, then polycarbonate or metal hardware is attached, and double-pane glass installed. A 0.9 × 1.2 m window weighs about 11 kg and uses perhaps 8 kg of PVC. With a single-screw extruder, an output of over 100 kg/h of lineals is considered very good in view of the close tolerances that must be maintained to obtain a tight seal and smooth operation. Double-hung, side-slide, and picture windows can be made of extruded PVC.

All the difficulties in achieving dark colors for PVC siding apply also to door and window frames and sashes. Coextrusion of a PVC core capped with a vinyl or acrylic film from an adjacent extruder can be used. In addition, PVC-acrylic alloys can be used for dark colors. The modifiers, stabilizers, and pigments incorporated in siding are used in these products as well. To date, building codes restrict their use in new construction, so that their installation is primarily as replacements.

Because of the extraordinary outdoor weatherability of ASA, it is being molded and extruded in various door and window frame applications. Likewise, in commercial construction, thermoplastic elastomers are finding increasing use in window-wall constructions. Poly(vinyl chloride) strips have been used as thermal breaks in aluminum windows, and aluminum doors and frames have been clad with PVC. A dual-wall, internally-ribbed construction, like that used for siding, has been used for door and window frames and sashes in mild climates.

Foams have limited use for these purposes. Rigid cellular PVC is good as a thermal barrier but not for structural parts. Doors and frames of structural molded foam, eg, foamed high impact polystyrene, can be made by injection molding, with recesses for hinges, striker plates, and miter corners. Solid polystyrene and structural foam-molded polyurethane have been molded for door frames.

Recently, storm doors have been constructed of advanced thermoplastic composites. Stampable, glass-mat reinforced polypropylene sheet is used to create a high strength outer skin. These compression molded skins are welded together using a friction or ultrasonic process then injection molded with a polyurethane foam core to produce an insulated structure. New technology for window frames incorporate the pultrusion of frame channels to produce a thermoset composite channel that can be filled with fiber glass for further insulation enhancement (12,31,33,34,48,49,54–56,60–67).

Wall and Ceiling Panels. Most panels incorporating plastics use foamed plastic cores with various surfacing materials for inside and outside facings. These facings may be an integral part of the panel or applied separately. The foam may be of polystyrene, polyurethane *[26778-67-6]*, polyisocyanurate, phenolic, or urea–formaldehyde *[9011-05-6]*. For some panels, expanded polystyrene beads are foamed in a large aluminum mold, with an accumulator feeding an injector of twenty or more nozzles. The foam has good moisture resistance and dimensional stability. Inserts and reinforcing materials, eg, glass fiber, steel rods, or wire mesh, have been used for greater strength. Door and window frames and conduits for services can be inserted during molding. After the foam is prepared, it is faced with a surfacing material for either interior or exterior exposures. Exterior facing may be wood, aluminum, vinyl, or plaster. Wall panels are used extensively for mobile homes. One panel uses polystyrene foam sheathing over the studs, covered by wood, aluminum, or vinyl siding. Polyurethane or urea–formaldehyde foam may be used between the studding. Gypsum board is used for the interior surface.

Roofing panels have been made from polyisocyanurate foams, both foam- and felt-reinforced with glass fiber. Phenolic resins are used especially for decorative laminates for paneling. The substrate may be fiberboard or a core of expanded polystyrene beads. In one case the beads are coated with phenolic resin, then expanded in a mold to form a structural foam panel.

In another application expanded polystyrene foam panels, 1.2 × 2.4 m, are faced with a wire mesh and mounted in a metal channel bolted to a concrete slab. These panels are then sprayed on both sides with plaster, which is anchored to the wire mesh and forms the interior and exterior surfaces. Roof and interior partitions provide low cost housing for mild climates.

Several companies have begun the mass production of foamed polyurethane wall panels as a modular product. Using a fully integrated computer-aided design (CAD) and manufacturing process, they are able to customize these panels by cutting them into tailored shapes including the insertion of doors and windows. This off-site manufacture of building components also aids the energy efficiency of finished, assembled structures by allowing a tight fit of modules to very close tolerances.

Even when plastics are not a preferred material for the structural element of paneling, they are often incorporated as a surface coating or sheet to enhance aesthetics. Some lay-in ceiling panels for commercial and institutional applications consist of gypsum board covered with a poly(vinyl chloride) surface sheet to add a textured appearance. Many more are based on gypsum board or mineral wall with a fiber glass or PVC surface.

An additional polystyrene panel application for one-piece structural building applications with high *R*-values is compatible with conventional wood framing. The panels may be used for load bearing walls up to three stories. Made from lumber facings and solid expanded polystyrene EPS insulation, the panels have the strength of a continuous column. A core of rigid EPS insulation 8.8 cm to 29 cm thick is adhesively welded between oriented strand board facings to form a structural panel that will not twist, warp, or be subject to racking.

Finally, a new aluminum fire-resistant paneling consists of a composite design that includes a solid thermoplastic compound core covered with a high density polyethylene adhesive film and an aluminum skin. The product is easily formable. It has sound deadening abilities, and an optional poly(vinylidene fluoride) resin coating provides damage resistance.

As a structural element to support paneling and wall mounts, there is growing interest in the use of plastic lumber produced using the recycled scrap or waste of polyethylene (HDPE), polypropylene, and PET materials from various packaging and other high turnover applications (12,17,18,21,23,24,32,34,44,62,68–71).

Plastic Flooring. Plastic flooring is marketed either as tile or sheet flooring. Tile is supplied as pieces usually 30.5 × 30.5 cm with a thickness of 0.16–0.32 cm and is usually homogeneous in composition. Sheet flooring, on the other hand, is produced in roll form 1.8, 2.7, 3.7 and 4.6 m wide (2- and 4-m in Europe), and generally consists of a plastic upper component on a fibrous backing.

Tile is based mainly on vinyl chloride and vinyl acetate copolymers. Some polypropylene tile systems have recently been introduced. A petroleum resin is usually employed as an extender and processing aid; conventional vinyl plasticizers and stabilizers also are incorporated. Reinforcing fibers and limestone constitute the remainder of the tile composition; the fibers contribute hot strength for processing and dimensional stability in the finished tile, limestone supplies bulk at an economical cost. Stable pigments are also incorporated. Since tile is installed on and below grade level, it is important that the finished product be resistant to the effects of moisture and alkali.

Tile is manufactured in several ways. In each method, a continuous sheet is formed; gauge refinement and planishing are carried out in subsequent calendering steps. Stresses that could lead to poor dimensional stability are avoided. The efforts to prevent stresses are governed by formulation, stock and roll temperatures, conveyor speeds, etc. After the final calendering, a resin–polymer–wax finish is applied to the surface of the sheet which is then buffed before it moves to the punch press. Frame scrap and tile rejected because of defects are returned to the mixers and recycled.

Several techniques are used to introduce decorative elements into tile. Random straight-graining effects are obtained by introducing pigmented, filled vinyl chips and granules, ie, mottle, into the tile composition at the appropriate point in the formation process. These flow to produce distinctive streaks as the sheet is formed. Less directional designs are produced by introducing grained vinyl chips, which form a continuous surface over a plain tile base. Random and registered designs are produced on a variety of tile bases by embossing and valley printing. Tile decorated by rotogravure printing is protected by a clear wear layer of plasticized PVC.

No-wax tile has long been important in the residential market. Such products have a high gloss surface coating that resists abrasion and soiling. When properly designed and maintained, no-wax tile retains its shiny appearance for an extended period of time without application of floor polish.

Resilient sheet flooring, though based on plasticized PVC, is manufactured from a variety of compositions by several processes. Generally, the type of decoration achieved depends on the process and composition. Since compositions are specific to processes, resilient sheet flooring can be classified by process alone. Rotogravure printing is used for the largest volume of sheet flooring. This type of flooring, often called rotovinyl, is manufactured almost exclusively from PVC plastisols and organosols. These liquid dispersions of homopolymer and plasticizer, when properly stabilized, can be applied as coatings that fuse into clear, tough films at temperatures of 180–200°C. Blowing agents can be incorporated to produce foams. Both clear coatings and foams are used in rotovinyl flooring. The typical structure consists of a fibrous inorganic or fiber glass backing, a vinyl foam layer decorated with a

rotogravure-printed design, and a clear vinyl surface layer. Many products of this type are embossed in register with portions of the design. Thickness varies from one product to another. Wear layers are 0.1–0.65 mm, depending on intended use, but the most common wear layer gauge is 0.25 mm. Rotovinyl flooring is produced in widths of 1.8, 2.7, 3.7, and 4.6 m. The fibrous backing is coated with a foamable plastisol containing a blowing agent. Clear plastisol is applied and the entire structure is heated enough to fuse the plastisols and cause expansion of the foamable gels. In this final step, embossing occurs by either chemical or mechanical means. The most widely used chemical technique involves a foaming inhibitor introduced in the appropriate inks.

In Europe, rotogravure flooring is made with a solid or foamed vinyl back; polyurethane froth also is used. A glass mat with urea–formaldehyde resin binder is incorporated for dimensional stability. Most U.S. rotovinyls are defined as no-wax floors, though only a few have a shiny polyurethane surface coating of 25–50 μm that aids in gloss retention and maintenance. Other rotogravure-decorated flooring contains opaque, translucent, or transparent vinyl chips embedded in the clear plastisol wear layer for added decoration. In Europe, rotary screen printers are used with vinyl plastisols to produce sheet flooring similar to that described as cushioned rotovinyl.

Stencil flooring is made 1.8 m wide on a similar fibrous inorganic fiber glass mat backing. It consists of granules of a mixture of PVC homopolymer and copolymer formulated with plasticizers, stabilizers, filler, and pigments to achieve the proper consistency for this process. These granules are deposited on the backing through automated stencils, each of which delivers a portion of the total design. The sheet moves intermittently, allowing time for the simultaneous deposition of granules from as many as 10 stationary stencils. The completed pattern is consolidated and embossed with heat and pressure in flatbed presses coordinated with the stencil line movement. This process is capable of a wide variety of designs that can extend through the thickness (ca 1 mm) of the deposited vinyl. A film of polyurethane is frequently applied to stencil sheet flooring to impart no-wax characteristics. A vinyl-backed product of this type has been introduced, combining rotogravure decoration with the stencil design and polyurethane surface.

Another 1.8-m wide sheet floor is made by a continuous process, called roll-press, on a similar felt backing by deposition of filled and pigmented vinyl granules or chips with subsequent consolidation in the nip between a steel pressure roll and a back-up roll. Most products of this type employ shaped or variegated vinyl chips oriented edge-to-edge in a monolayer, with clear vinyl filling the spaces between them. The chips are formulated from homopolymers of PVC with as much as 65% limestone. Dry-blend, used as mortar between the chips, is made from suspension polymers of PVC in mixers that allow the absorption of plasticizers and other liquid components at relatively low temperatures so that free-flowing dry powders result. Wear layer thicknesses vary between 0.8 and 1.3 mm (30 and 50 mils). Some of these products are coated with polyurethane for gloss retention and easier maintenance (72–74).

Pipe. Plastic pipe can be made for pressure uses such as potable water supply, gas pipelines, and pressurized sewers, or for nonpressure uses such as other sewers, drains-waste-vent (DWV), and other drainage. For some time, high density polyethylene was used most widely, with ABS preferred for DWV. In the last decade, use of PVC in piping has grown and now represents over 75% of the material used for pipe, fittings, and conduit. Over 40% of the North American consumption of PVC is used for this market with demand anticipated to reach 2 million metric tons by 1994. Pipe for potable water may be made from PVC or polybutylene. However, negative publicity regarding polybutylene piping when used in conjunction with polyacetal fittings has hurt the market prospects for this system. High molecular weight, high density polyethylene (HDPE) is used for pressurized sewer lines, up to 0.7 MPa (100 psi). A resin of molecular weight 75,000–90,000 is preferred; it is compounded with tin stabilizers and a mixture of lubricants, and blended in a high speed mixer to obtain a uniform dry blend. Multiple-screw extruders, 8–13 cm in diameter, mix and push the compound through a die designed to give a streamline, not turbulent, flow at a rate of 500–1600 kg h. Impact modifiers of acrylic or ABS resins are added to reduce breakage and provide better performance under pressure.

Chlorinated PVC (CPVC) is preferred in some cases, especially in mobile and site-constructed homes, for hot water pipe because it is stable to 88°C at 0.7 MPa (100 psi). Polybutylene is also good for hot water lines and has the advantage of flexibility. Chlorinated PVC can be solvent-welded, whereas polybutylene must be mechanically clamped or heat-welded. In some cases, fittings of chlorinated PVC or polyacetal can be connected to polybutylene. High density polyethylene is extruded through single-screw extruders, which are lower in cost and have a higher output rate. ABS resin can be used for pressurized applications, such as gas and water lines, where adverse conditions are met. For extreme pressure conditions, PVC pipe may be filament-wound or overwrapped with glass-fiber tape and impregnated with a polyester or an epoxy resin to provide the much greater bursting strength required for municipal water pipe when relatively thin-walled PVC pipe is used.

For nonpressure conditions, a greater variety of resins and production processes is available. One of the largest uses is for DWV piping; the principal resins are ABS and PVC modified with ABS to improve its impact resistance. The pipe may be cut or sawed and is solvent-welded readily with an ABS cement. Foamed ABS pipe has a lighter weight and lower cost and it has a closed-cell structure with a solid skin. Two extruders are used, one for the surfaces and one for the core, which may be of a different and possibly lower cost resin. Both the skin thickness and the core density can be accurately controlled. The pipe is more rigid and lower in cost than solid ABS pipe of the same diameter, but it also has lower tensile strength. PVC and HDPE also can be foam-extruded for the same purposes, with similar advantages and limitations. These pipes can be used for sewers and drains.

Overall, improvements in processing technology and material properties will propel the continued growth of plastic pipe. Further penetrations into markets such as sewer mains and chemical process piping will come from making pipe with greater strength and better tolerance to temperature extremes, pressure, and corrosion. Cost considerations are a primary factor when choosing materials for piping. Building contractors save up to 30 cents on every dollar by using PVC pipe because of material, installation, and labor cost advantages. CPVC plumbing pipe systems cost up to 25% less than copper in new hot and cold water installations. When PVC is compared to cast-iron soil pipe in drain, waste, and vent pipe installations, savings vary from 10 to 25%. Because of the cost advantages and long life, PVC commands over three-fourths of the plastic pipe market and is expected to maintain its position well into the next century. Barriers to growth include the fact that PVC is not approved in some municipal codes for use in pressure situations. With no single national code authority, fragmentation has occurred as a result of regional, state, and local codes that reflect different geographical requirements. In many situations, the type of pipe required will be specified by a professional engineer, who has more experience with iron and concrete.

Ductile iron pipe makers realize their best returns in the greater than 10-cm (4-in.) pipe market, and in fittings, flanges, and valves where PVC is not widely used. Since fittings made of PVC are generally not accepted in the engineering community, ductile iron makers enjoy the advantage of being able to supply a full product line. The concrete sewer pipe market is more vulnerable to penetration by PVC pipe. Advances in ribbed, foam core, channel core and truss pipe enable PVC to compete in larger-diameter markets. Unlike the pressure pipe market where PVC is generally not price competitive above 30 cm, this new sewer pipe technology pushes PVC up into the 45–75 cm range.

While concrete pipe will have trouble being cost competitive, its poor corrosion-resistant properties can be overcome with the use of PVC liners, putting it in a position to compete against PVC pipe on its superior crush resistance. The more recent news in PVC and HDPE pipe manufacturing is geared toward materials saving, as the price of resin has risen dramatically. PVC foam-core pipe reduces material consumption up to 40% and tooling is currently applicable to DWV pipe from 1–20-cm (0.5 to 8-in.) diameters. Small-diameter, aluminum-reinforced, cross-linked HDPE pipe consists of an aluminum tube sandwiched between inner and outer layers of cross-linked HDPE. Current availability is for diameters of 1–20 cm. This pipe is impermeable to gas, immune to corrosion, and is easier to blend and install than either all-aluminum or all-HDPE pipe. It is rated to 1 MPA (150 psi) at temperatures over 90°C, making it applicable for closed indoor heating systems. Two new types of corrugated pipe with smooth inner bores, each produced by a proprietary system, have now met all specifications for sewer pipe and are said to provide material savings of up to 50% over conventional PVC pipe (40,75,76).

Plumbing and Bathroom Fixtures. Plastics for fittings such as faucet handles, shower heads, and plumbing parts must have high strength and resistance to creep, abrasion, and dimensional change, especially when exposed to moisture. ABS resin is widely used for these purposes, and for soap dispensers, water filters, and other accessories. The article can be chrome-plated or color can be molded in. Polyacetal can also be used for these articles as well as for valves, couplings, and pumps where its natural self-lubricity is an advantage. Polycarbonate may be injection-molded to form handles and other parts, which can be connected by a press fit instead of by threaded lock-nuts, as required for metal.

Sanitary ware, including tubs, showers, combined units, basins, and toilet tank, may be made of thermoformed ABS or acrylic sheet, molded glass-fiber-reinforced polyester, or cast acrylic resins. The glass-polyester type dominates the tub shower market. It is possible to install the units as a two-component system, assembled in place. Gel coats may be of thermoformed decorative acrylic skins. To reduce the smoke generated by fire, methyl

methacrylate can be substituted for the styrene in the polyester and alumina trihydrate used as a fire-retardant filler. Marble chips and dust can be included in the formulation to give a cultured-marble product for vanities, tubs, and panels. Thermoformed acrylic is usually given a glass–polyester backing which is sprayed on, or the acrylic and backing are press-molded together. A thermosetting acrylic filled with marble chips and dust is cast in an aluminum mold, cured to achieve cross-linking, then postcured to obtain a cultured marble basin, tub shower unit, or paneling. It may be a polished or matte finish with a great variety of colors and patterns.

By a casting process using about one-third acrylic resin, usually methyl methacrylate, and two-thirds ATH, integrated counter top bowl units and sheet can be fabricated. These marblelike products are very durable, both retaining their initial appearance and having a renewable surface.

The do-it-yourself market has been largely fueled by plumbing product sales. Consumers have been spending more on bath and kitchen remodeling, where it is viewed as an investment. The overall growth in the market is because of rising consumer incomes, replacements, additions, alterations, and growth in niche markets such as designer and plastic fixtures and fittings. Plastic fixtures, unlike porcelain, are easy to mold in any color, and can be made an integral part of a well-designed kitchen or bath. The use of plastics in plumbing expanded from 20% to 32% between 1977 and 1989 with plastic and glass-fiber-reinforced plumbing fixtures accounting for nearly 50% of plumbing fixtures in 1990 (5,12,17,40,77–83).

Toxicity

Indoor Air Quality. Indoor air quality has become a greater concern since the energy crisis of the early 1970s as buildings have become more energy efficient and airtight. A number of real and potential health hazards regarding air quality have been debated including radon, tobacco smoke, asbestos, formaldehyde, volatile organic compounds (VOCs), and combustion by-products from stoves and furnaces. With regard to plastics, urea–formaldehyde insulating foams have received the greatest publicity. In the early to mid-1980s, they were studied for their formaldehyde release, ie, outgassing. The U.S. EPA has set an acceptable level of formaldehyde within indoor air at 0.1 ppm. Another potential source of formaldehyde release in buildings is from the binder systems, such as phenol–formaldehyde and urea–formaldehyde, used in pressed wood products such as particle board (84,85).

Smoke Toxicity of Burning Plastics. Smoke, not flames, is the primary cause of death in most fires. However, past efforts to determine which building product components, eg, wood, fabric, plastic, etc, generate the most harmful or toxic smoke emissions have proven inconclusive. The National Institute of Building Sciences (NIBS) lists seven factors that contribute to the overall risk danger of materials' combustion toxicity: (*1*) ease of ignition; (*2*) flame spread; (*3*) fire endurance or how rapidly fire penetrates a barrier; (*4*) rate of heat rise; (*5*) ease of fire extinction; (*6*) smoke evolution; and (*7*) toxic-gas generation. NIBS has noted that combustion toxicity is not just a building materials issue but also a building products design issue. At present, several state, eg, New York, and local governments have enacted legislation requiring the testing and filing of smoke toxicity data for all building construction products used within their jurisdiction. However, because these tests, such as the Pittsburgh Test developed at the University of Pittsburgh, measure an arbitrary value of toxicity, typically on mice under short-term laboratory conditions excluding long-term chronic health effects or teratological factors, no effort has been successful at linking these test data to a meaningful set of building code regulations. NIBS is currently working to develop a nationally recognized standard for measuring combustion toxicity that it will present to ASTM. Finally, several companies are developing proprietary wall coverings that trigger ionization-type smoke detectors early in the thermal cycle of a fire. This pre-alert capability will further enhance the safety of buildings from the risk of fire (84,86,87).

Additive Toxicity. Plastic building products almost always incorporate additives such as colorants, plasticizers, uv light stabilizers, and flame retardants. Several families of these various additives are under increasing regulatory scrutiny for their potential risks with regard to smoke toxicity and their effects upon worker health in compounding processing plants. In Europe, there is currently an effort by Germany to have the EEC regulate the use of poly(brominated diphenyl oxide) (PBDPO) flame retardants because of their suspected risks when inhaled by workers. Antimony oxide, an effective synergist with other flame retardants, is also under review in several locations though no regulatory actions are pending. Additionally, chlorinated flame retardants are being reviewed for their likelihood to generate hydrochloric (HCl) gas upon combustion. Most heavy-metal colorants, eg, those based on cadmium, lead, and cobalt, are also being reviewed for safety; in many cases, alternative colorants are available (88,89).

Engineering and Recycled Plastics

The plastic building materials industry is facing rapid change and the accelerated use of engineering and recycled plastics is one catalyst for this change. Engineering thermoplastics have better mechanical properties than commodity plastics. For instance, polypropylene sheet melts at temperatures under 100°C, whereas temperatures in excess of 150°C are required to melt most engineering thermoplastics. Thermoplastics can be combined with fibers, fillers, and traditional building materials like concrete or wood, creating composite materials with special performance features such as durability, fireproofing, and stress resistance. Plastic products account for less than 10% of the materials used to make a typical U.S. home today. Despite this limited market penetration, building and construction uses are the second largest market (behind packaging) for plastic resin. Resin demand for building and construction is expected to double by the year 2000, to about 14 million metric tons.

The Dow Chemical Company, General Electric (GE), Monsanto, and many other companies have focused their efforts on opportunities for plastic in the building and construction industry. The Dow Chemical Company offers a wide range of products, including Styrofoam extruded polystyrene foam board insulation and a series of construction-related engineering resins designed for OEM, converter, and fabricator applications. Its polycarbonate blends resist warping and have high dimensional stability and a low coefficient of thermal expansion for use in exterior large-sheet applications, such as doors and siding. Exterior products thermoformed from The Dow Chemical Company resins can be stained or painted like wood after being subjected to a new surface treatment technology.

GE has invested $10 million to build a 300-square meter residence in Pittsfield, Massachusetts, that will use over 20,000 kilograms of resin, accounting for 30% of all the building materials used in this structure. Resins are used in the roof, windows, siding, plumbing, foundation, and electrical system. In the design for the radiant interior wall, laminated panels do three fundamental jobs: divide space; allow for service distribution such as water, electricity, and control networks; and provide heating and cooling. The core of the panel is extruded low density poly(phenylene oxide) foam; skins are of glass-reinforced thermoplastic. Through the core runs a vertical channel that houses water and gas pipe and wiring and also serves as supply and return duct for air.

Other innovative applications for plastics have recently been introduced into the construction market. For example, reinforced-thermoplastic urethane joints and reinforced-vinyl ester structural rods are being incorporated into lightweight scaffolding. The new components prevent rust and resist chemical attack. The joints are injection molded of rigid thermoplastic urethane. The material is said to have the impact strength needed to withstand the force of joints being dropped to the ground when the scaffolding is being dismantled. A composite reinforcement material, aimed at replacing steel rod reinforcements in concrete, is made from aramid (aromatic polyamide) and carbon fibers (qv) that have been braided together and then impregnated with a resin to form stiff rods. Braiding adds to the overall mechanical strength of the composite and also creates surfaces that form tight bonds with concrete. This material is only one-sixth the weight of iron reinforcement materials, but its strength is said to be five to six times as great. Ultrahigh molecular weight polyethylene (UHMWPE) molds are replacing wood-slat molds for brickmaking. These UHMWPE molds have a longer life, boost productivity, and reduce maintenance costs without sacrificing the character of the bricks. Fiber glass studs and nuts have developed a specialty market in structures that must be nonconductive or chemical- and corrosion-resistant. Pultruded glass-reinforced vinyl ester fasteners are used in structures that house underwater cameras in the assembly of geodesic panels that form a radome and are used in the construction of chemical plants.

Recycled plastic products have just recently been introduced in the construction market, primarily for exterior use. Eventually, recycled plastics may represent one-half of the thermoplastics in a commercially-made home. Milk and detergent bottles, scrap generated by extruders and molders, and scrap from the manufacture of engineering plastics are being combined and processed into lumber. Various resins, including high density polyethylene and styrene-based engineering plastics, are processed in a specially designed extruder and the lumber is used for landscaping, retaining walls, sign posts, and fencing. Recycled plastic from fast-food containers and soda bottles is being made into insulation, which its producer claims is safe from both toxicological and environmental standpoints (10,31,90).

Emerging Developments

A very high price and performance family of polymers called liquid crystal polymers (LCPs) exhibit extremely high mechanical and thermal properties. As their ease of processing and price improve, they may find application in thin-wall, high strength parts such as nails, bolts, and fasteners where metal parts cannot be used for reasons of conductivity, electromagnetic characteristics, or corrosion.

Thermoset polyurethane as a binder material for gravel systems is also under development. Applications could include roofing systems that require a high degree of uv light and abrasion resistance.

Certain state highway authorities are studying the use of fiber-reinforced polymers, typically thermosets such as epoxy or unsaturated polyester, for bridge construction. On an even more futuristic scale, fiber optics that employ polymeric jacketing and, in some cases, optically active polymeric cores, may someday be employed in place of wires for home security systems, climate control, etc (10,91).

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BUTADIENE

Butadiene, C_4H , exists in two isomeric forms: 1,3-butadiene *[106-99-0]*, $CH_2{=}CH\ \ CH{=}CH_2$, and 1,2-butadiene *[590-19-2]*, $CH_2{=}C{=}CH\ \ CH_3$. 1,3-Butadiene is a commodity product of the petrochemical industry with a 1989 U.S. production of 3.1 billion pounds (1.4×10^9 kg) according to the United States International Trade Commission (USITC) (1). Although this is not very different from the production in 1971, it represents significant rebound from the low production in the mid-1980s. Elastomers consume the bulk of 1,3-butadiene, led by the manufacture of styrene—butadiene rubber (SBR). 1,3-Butadiene is manufactured primarily as a coproduct of steam cracking to produce ethylene in the United States, Western Europe, and Japan. However, in certain parts of the world (eg, China, India, Poland, and the former Soviet Union) it is still produced from ethanol. The earlier manufacturing processes of dehydrogenation of *n*-butane and oxydehydrogenation of *n*-butenes have significantly declined in importance and output. Efforts have been made to make butadiene from other feedstocks such as other hydrocarbons, coal (2,3), shale oil (4), and renewable sources like animal and vegetable oil (5), cellulose, hemicellulose, and lignin (6,7), but in the United States none of these have moved beyond the research and development stage.

The other isomer, 1,2-butadiene, a small by-product in 1,3-butadiene production, has no significant current commercial interests. However, there are a number of publications and patents on its recovery and applications, particularly in the specialty polymer area (8,9) and as a gel inhibitor (10).

Properties

1,3-Butadiene is a noncorrosive, colorless, flammable gas at room temperature and atmospheric pressure. It has a mildly aromatic odor. It is sparingly soluble in water, slightly soluble in methanol and ethanol, and soluble in organic solvents like diethyl ether, benzene, and carbon tetrachloride. Its important physical properties are summarized in Table 1 (see also references 11, 12). 1,2-Butadiene is much less studied. It is a flammable gas at ambient conditions. Some of its properties are summarized in Table 2.

Table 1. Physical Properties of 1,3-Butadiene[a]

Property	Value
CAS Registry Number	*[106-99-0]*
RTECS accession number	EI9275000
UN number	1010
molecular formula	C_4H
molecular weight	54.092
boiling point at 101.325 kPa[b], °C	4.411
freezing point, °C	108.902
critical temperature, °C	152.0
critical pressure, MPa[c]	4.32
critical volume, cm^3 mol	221
critical density, g mL	0.245
density (liquid), g mL at	
0°C	0.6452
15°C	0.6274
20°C	0.6211
25°C	0.6194
50°C	0.5818
density (gas) (air 1)	1.9
heat capacity at 25°C, J (mol·K)[d]	79.538
refractive index, n_D at 25°C	1.4292
solubility in water at 25°C, ppm	735[e]
viscosity (liquid), mPa·s (cP) at 40°C	0.33
0°C	0.25
40°C	0.20
heat of formation, gas, kJ mol[d]	110.165
heat of formation, liquid, kJ mol[d]	88.7
free energy of formation, kJ mol[d]	150.66
heat of vaporization, J g[d] at	
25°C	389
boiling point	418
flash point, °C	85
autoignition temperature, °C	417.8
explosion limits in air, vol %	
lower	2.0
upper	11.5
minimum oxygen for combustion (MOC), % v/v O_2	

N_2–air	10
CO_2–air	13
absorption	
λ, cm^{-1}	217
log ε	4.32

[a] Refs. 22–28.

[b] To convert kPa to mm Hg, multiply by 7.5.

[c] To convert MPa to psi, multiply by 145.

[d] To convert J to cal, divide by 4.184.

[e] 245 mol ppm.

Table 2. Physical Properties of 1,2-Butadiene[a]

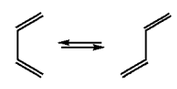
Property	Value
CAS Registry Number	*[590-19-2]*
molecular formula	C_4H
molecular weight	54.092
boiling point at 101.325 kPa,[b] °C	10.85
freezing point, °C	136.19
density (liquid), g mL at	
0°C	0.676
20°C	0.652
heat of formation at 25°C (gas), kJ mol[c]	162.21
heat of vaporization at 25°C, kJ mol[c]	23.426
refractive index at 1.3°C	1.4205

[a] Refs. 24, 29.

[b] To convert kPa to mm Hg, multiply by 7.5.

[c] To convert kJ to kcal, divide by 4.184.

1,3-Butadiene, the simplest conjugated diene, has been the subject of intensive theoretical and experimental studies to understand its physical and chemical properties. The conjugation of the double bonds makes it 15 kJ mole (3.6 kcal mol) (13) more thermodynamically stable than a molecule with two isolated single bonds. The *s*-trans isomer, often called the trans form, is more stable than the *s*-cis form at room temperature. Although there is a 20 kJ mole (4.8 kcal mol) rotational barrier (14,15), rapid equilibrium allows reactions to take place with either the *s*-cis or *s*-trans form (16,17).



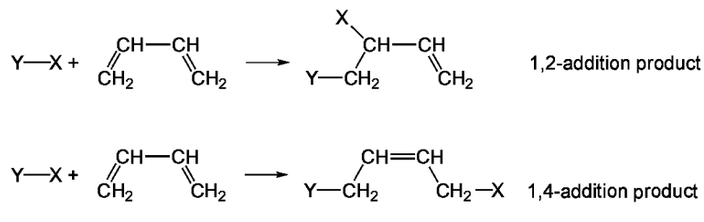
The double-bond length in 1,3-butadiene is 0.134 nm, and the ingle-bond, 0.148 nm. Since normal carbon–carbon single bonds are 0.154 nm, this indicates the extent of double-bond character in the middle single-bond. Upon complexing with metal carbonyl moieties like $Fe(CO)_3$, the two terminal bonds lengthen to 0.141 nm, and the middle bond shortens even more to 0.145 nm (18).

Solubilities of 1,3-butadiene and many other organic compounds in water have been extensively studied to gauge the impact of discharge of these materials into aquatic systems. Estimates have been advanced by using the UNIFAC derived method (19,20). Similarly, a mathematical model has been developed to calculate the vapor–liquid equilibrium (VLE) for 1,3-butadiene in the presence of steam (21).

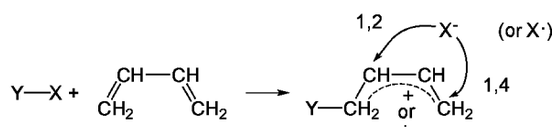
Reactions

Since the discovery of 1,3-butadiene in the 19th century, it has grown into an extremely versatile and important industrial chemical (30). Its conjugated double bonds allow a large number of unique reactions at both the 1,2- and 1,4-positions. Many of these reactions produce large volumes of important industrial materials.

Addition Reactions. 1,3-Butadiene reacts readily via 1,2- and 1,4-free radical or electrophilic addition reactions (31) to produce 1-butene or 2-butene substituted products, respectively.

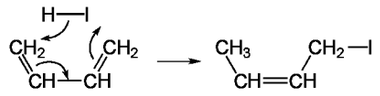


The intermediate in these reactions in the case of the addition of YX is consistent with the addition of Y to the 1-position to form an allylic intermediate to which X adds to produce either the 1,2- or 1,4-product.



The addition of HX, where X is a halogen, has been thoroughly investigated (32,33). Whether 1,2- or 1,4-product dominates depends on reaction

conditions. For instance, although HCl adds to butadiene at low temperatures to produce 75–80% of the 1,2-addition product, the thermodynamically more stable 1,4-isomer is favored at higher temperatures (34). On the other hand, HI has been shown to add to butadiene in the vapor phase by a pericyclic mechanism to produce the 1,4-product (35).



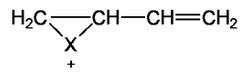
Addition of water (36) or alcohols (37–39) directly to butadiene at 40–100°C produces the corresponding unsaturated alcohols or ethers. Acidic ion exchangers have been used to catalyze these reactions. The yields for these latter reactions are generally very low because of unfavorable thermodynamics. At 50°C addition of acetic acid to butadiene produces the expected butenyl acetate with 60–100% selectivity at butadiene conversions of 50%. The catalysts are ion-exchange resins modified with quaternary ammonium, quaternary phosphonium, and ammonium substituted ferrocenyl ions (40). Addition of amines yields unsaturated alkyl amines. The reaction can be catalyzed by homogeneous catalysts such as $Rh[P(C_6H_5)_3]_3Cl$ (41) or heterogeneous catalysts such as MgO and other solid bases (42).

The manufacture of hexamethylenediamine *[124-09-4]*, a key comonomer in nylon-6,6 production proceeds by a two-step HCN addition reaction to produce adiponitrile *[111-69-3]*, $NCCH_2CH_2CH_2CH_2CN$. The adiponitrile is then hydrogenated to produce the desired diamine. The other half of nylon-6,6, adipic acid (qv), can also be produced from butadiene by means of either of two similar routes involving the addition of CO. Reaction between the diamine and adipic acid *[124-04-5]* produces nylon-6,6.

The first CO route to make adipic acid is a BASF process employing CO and methanol in a two-step process producing dimethyl adipate *[627-93-0]* which is then hydrolyzed to the acid (43–46). Cobalt carbonyl catalysts such as $Co_2(CO)_8$ are used. Palladium catalysts can be used to effect the same reactions at lower pressures (47–49).

The other CO route for adipic acid manufacture involves 1,4-addition of CO and O_2 to butadiene to produce an intermediate, which is subsequently hydrogenated and hydrolyzed to adipic acid (50). This is called the oxycarbonylation process. Both the BASF and the oxycarbonylation processes have been intensively investigated.

Halogenation of butadiene has also attracted a lot of interest. Both 1,2- and 1,4-isomers are formed. Since the *trans*-1,4-isomer was observed from the 1,4-addition product, researchers postulate that the the electrophilic X^+ forms a 1,2-cyclic intermediate and not a 1,4-cyclic intermediate that would form the *cis*-1,4-addition product (51,52).

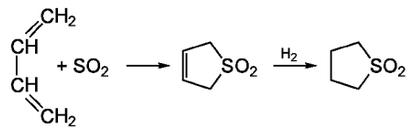


Fluorination with XeF_2 or $C_6H_5IF_2$ gives both the 1,2- and 1,4-difluoro products. This reaction proceeds via the initial electrophilic addition of F^+ to the diene (53).

Chloroprene (qv), 2-chloro-1,3-butadiene, *[126-99-8]* is produced commercially from butadiene in a three-step process. Butadiene is first chlorinated at 300°C to a 60:40 mixture of the 1,2- and 1,4-dichlorobutene isomers. This mixture is isomerized to the 3,4-dichloro-1-butene with the aid of a $Cu–Cu_2Cl_2$ catalyst followed by dehydrochlorination with base such as NaOH (54).

The 1,4-dichloro-2-butene can also be separated and hydrolyzed with aqueous NaOH to form 1,4-butenediol, which is hydrogenated with Ni catalyst to produce 1,4-butanediol. In 1971 this process was commercialized in Japan (55). The plant is now shut down because of unfavorable economics.

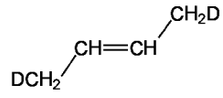
Butadiene also undergoes a 1,4-addition reaction with SO_2 to give sulfolene *[77-79-2]*. This reaction followed by hydrogenation is commercially used to manufacture sulfolane *[126-33-0]* (56).



Formaldehyde also reacts with butadiene via the Prins reaction to produce pentenediols or their derivatives. This reaction is catalyzed by a copper-containing catalyst in a carboxylic acid solution (57) or $RuCl_3$ (58). The addition of hydrogen also proceeds via 1,2- and 1,4-addition.

Hydrogenation Reactions. Butadiene can be hydrogenated to *n*-butanes and *n*-butane using a large number of heterogeneous (59) and homogeneous (60–64) catalysts. Palladium-containing membranes have also been used to allow the use of permeated hydrogen to effect hydrogenation (65–67). Many catalysts have been developed and used commercially to remove small quantities (~3%) of butadiene from 1-butene streams (68–71). Since 2-butene *[107-01-7]* is more stable thermodynamically than 1-butene *[106-98-9]* under mild conditions, catalysts that promote 1,2-addition and do not isomerize 1-butene are essential for getting high 1-butene selectivity. Many of the palladium catalysts require the use of CO to improve 1-butene selectivity (72–74).

Selectivities to various isomers are more difficult to predict when metal oxides are used as catalysts. ZnO preferentially produced 79% 1-butene and several percent of *cis*-2-butene *[624-64-6]* (75). CdO catalyst produced 55% 1-butene and 45% *cis*-2-butene. It was also reported that while interconversion between 1-butene and *cis*-2-butene was quite facile on CdO, cis–trans isomerization was slow. This was attributed to the presence of a π-allyl anion intermediate (76). High *cis*-2-butene selectivities were obtained with molybdenum carbonyl encapsulated in zeolites (77). On the other hand, deuteration using ThO_2 catalyst produced predominantly the 1,4-addition product, *trans*-2-butene-d_2 with no isotope scrambling (78).



Although supported Pd catalysts have been the most extensively studied for butadiene hydrogenation, a number of other catalysts have also been the object of research studies. Some examples are Pd film catalysts, molybdenum sulfide, metal catalysts containing Fe, Co, Ni, Ru, Rh, Os, Ir, Pt, Cu, MgO, $HCo(CN)_5^{3-}$ on supports, and $LaCoO_3$ Perovskite. There are many others (79–85). Studies on the well-characterized Mo(II) monomer and Mo(II) dimer on silica carrier catalysts have shown wide variations not only in catalyst performance, but also of activation energies (86).

Another method to hydrogenate butadiene occurs during an oxidation–reduction reaction in which an alcohol is oxidized and butadiene is reduced. Thus copper–chromia or copper–zinc oxide catalyzes the transfer of hydrogen from 2-butanol or 2-propanol to butadiene at 90–130°C (87,88).

Oxidation Reactions. Like all reactions between oxygen and hydrocarbons, complete oxidation of butadiene is controlled by limiting the oxygen and operating at specific temperature ranges. Other ways to control selectivity to specific products involve the use of catalysts and or conducting the reaction in the presence of other reagents. Some of the many oxidized products are depicted in Figure 1.

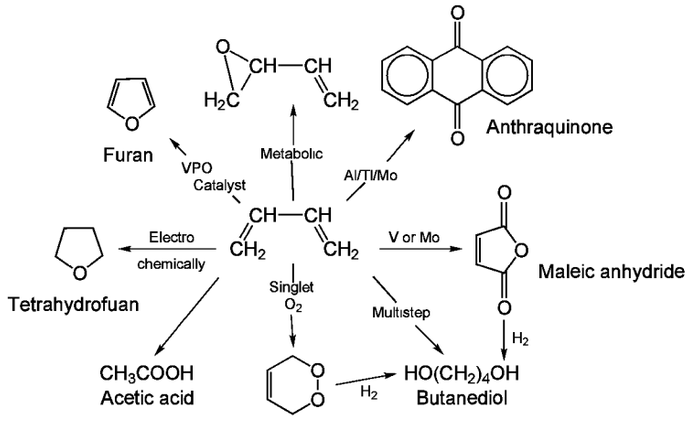


Fig. 1. Oxidative reactions of butadiene.

The vapor-phase oxidation (VPO) of butadiene with air at 200–500°C produces maleic anhydride *[108-31-6]*. Catalysts used are based on vanadium and molybdenum oxides (89,90). Alternatively, when using a catalyst containing Al, Mo, and Ti, butadiene undergoes a complex series of condensations and oxidations to form anthraquinone at 250°C (91).

Reaction between oxygen and butadiene in the liquid phase produces polymeric peroxides that can be explosive and shock-sensitive when concentrated. Ir(I) and Rh(I) complexes have been shown to catalyze this polymerization at 55°C (92). These peroxides, which are formed via 1,2- and 1,4-addition, can be hydrogenated to produce the corresponding 1,2- or 1,4-butanediol *[110-63-4]* (93). Butadiene can also react with singlet oxygen in a Diels-Alder type reaction to produce a cyclic peroxide that can be hydrogenated to 1,4-butanediol.

Oxygen has also been shown to insert into butadiene over a VPO catalyst, producing furan *[110-00-9]* (94). Under electrochemical conditions butadiene and oxygen react at 100°C and 0.3 amps and 0.43 volts producing tetrahydrofuran *[109-99-9]*. The selectivity to THF was 90% at 18% conversion (95). THF can also be made via direct catalytic oxidation of butadiene with oxygen. Active catalysts are based on Pd in conjunction with polyacids (96), Se, Te, and Sb compounds in the presence of Cu_2Cl_2, $LiCl_2$ (97), or Bi–Mo (98).

The oxidation reaction between butadiene and oxygen and water in the presence of CO_2 or SO_2 produces 1,4-butenediol. The catalysts consist of iron acetylacetonate and LiOH (99). The same reaction was also observed at 90°C with Group (VIII) transition metals such as Pd in the presence of I_2 or iodides (100). The butenediol can then be hydrogenated to butanediol *[110-63-4]*. In the presence of copper compounds and at pH 2, hydrogenation leads to furan (101).

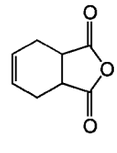
Alternatively, butadiene can be oxidized in the presence of acetic acid to produce butenediol diacetate, a precursor to butanediol. The latter process has been commercialized (102–104). This reaction is performed in the liquid phase at 80°C with a Pd–Te–C catalyst. A different catalyst system based on $PdCl_2(NCC_6H_5)_2$ has been reported (105). Copper- (106) and rhodium- (107) based catalysts have also been studied.

$$CH_2{=}CH{-}CH{=}CH_2 + 2\,CH_3COOH + O_2 \rightarrow CH_3COOCH_2CH{=}CHCH_2OOCCH_3 \xrightarrow{2\,H_2}$$
$$CH_3COOCH_2CH_2CH_2CH_2OOCCH_3 \xrightarrow{H_2O} HOCH_2CH_2CH_2CH_2OH + 2\,CH_3COOH$$

Another butadiene oxidation process to produce butanediol is based on the 1,4-addition of *t*-butyl hydroperoxide to butadiene (108). Cobalt on silica catalyzes the first step. This is followed by hydrogenation of the resulting olefinic diperoxide to produce butanediol and *t*-butyl alcohol.

Butadiene can also be readily epoxidized with peracids to the monoepoxide or the diepoxide (109,110). These have been proposed as important intermediates in the metabolic cycle of butadiene in the human body (111).

Diels-Alder Reactions. The important dimerization between 1,3-dienes and a wide variety of dienophiles to produce cyclohexene derivatives was discovered in 1928 by Otto Diels and Kurt Alder. In 1950 they won the Nobel prize for their pioneering work. Butadiene has to be in the *s*-cis form in order to participate in these concerted reactions. Typical examples of reaction products from the reaction between butadiene and maleic anhydride (1), or cyclopentadiene (2), or itself (3), are *cis*-1,2,3,6-tetrahydrophthalic anhydride *[27813-21-4]*, 5-vinyl-2-norbornene *[3048-64-4]*, and 4-vinyl-1-cyclohexene *[100-40-3]*, respectively.



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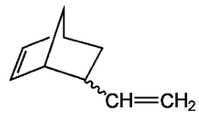

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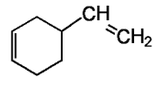


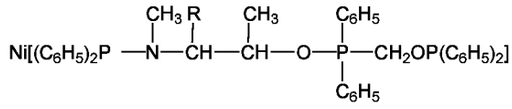
(3)

Diels-Alder reactions with butadiene are generally thermally reversible and can proceed in both gas and liquid phases. The reactions are exothermic and follow second-order kinetics; first-order with respect to each reactant.

The dienophiles for reaction with butadiene can be alkenes, allenes, and alkynes. Simple alkenes like ethylene are poor dienophiles resulting in sluggish reactions. Substituted olefins, X—C=C—X′, are more reactive when X and/or X′ are C=C, Ar, COOR, COOH, COH, COR, COCl, CN,

halogens, and many other electron-withdrawing substituents (112–116). A compilation of the reaction parameters between butadiene and C2–C4 olefins in the temperature range of 510–750°C has been published (117). Other double-bond or triple-bond compounds, such as C=N–, –N=N–, O=C–, C≡N, and O_2 can also act as dienophiles to give heterocyclic products. These reactions have been the subject of extensive orbital symmetry studies (118,119).

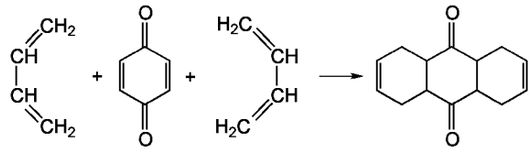
Diels-Alder reactions are thermal reactions requiring no catalysts (120). However, over the years both acid- and metal-based homogeneous or heterogeneous catalysts have been developed (121–127). Some catalysts used in Diels-Alder catalyzed reactions of butadiene are $Fe(NO)_2Cl$–$(CH_3CH_2)_2AlCl$, $Pd[P(C_6H_5)_3]_4$, Cu(I) exchanged silica–alumina (128,129), large pore zeolites (130), and carbon molecular sieves. An electrochemical process has also been used to catalyze the self-condensation to vinylcyclohexene (131). When the asymmetric Ni catalyst (4) was used, specificity to the enantomeric (*S*)-4-vinylcyclohexene (132,133) was observed (26% enantiomeric excess).



(4)

When the Diels-Alder reaction between butadiene and itself is carried out in the presence of alkali metal hydroxide or carbonate (such as KOH, Na_2CO_3, and K_2CO_3 on alumina or magnesia supports) dehydrogenation of the product, vinylcyclohexene, to ethylbenzene can occur at the same time (134). The same reaction can take place on simple metal oxides like ZrO_2, MgO, CaO, SrO, and BaO (135).

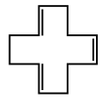
The Diels-Alder reaction between two moles of butadiene and one mole of quinone *[106-51-4]* produces tetrahydroanthraquinone *[28758-94-3]* (136).



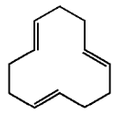
Dimerization and Oligomerization Reactions. Besides Diels-Alder-type dimerization reactions, butadiene undergoes a number of other dimerization or oligomerization reactions to produce cyclic or linear products. With the proper catalysts these reactions proceed quite selectivity. Noncatalyzed or photocatalyzed dimerizations produce compounds like divinylcyclobutanes and have been studied in detail (137,138).

A fascinating series of cyclodimerization or cyclotrimerization reactions was first observed in the labs of Wilke to produce 1,5-cyclooctadiene *[111-78-4]* (COD) and *cis,trans,trans*-1,5,9-cyclododecatriene *[2765-29-9]* (CTT), or *trans,-trans,trans*-1,5,9-cyclododecatriene *[676-22-2]* (TTT).

COD



CTT



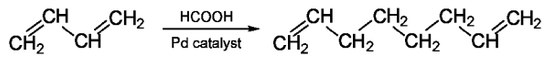
TTT

These cyclodimerization and cyclotrimerization reactions are catalyzed by low valent Ziegler-type Ni catalysts (139–144). Large ligands, such as tris-o-biphenylyl phosphite on nickel tend to favor cyclooctadiene (COD) formation while smaller ligands favor the linear dimer, 1,3,7-octatriene. The dimer yield at 80°C and 101.3 kPa (1 atm) is 96%. The nickel catalyst can also be placed on a support so that it can be recycled (145). Many other type catalysts have been reported for this reaction (146). The linear 1,3,7-octatriene and its 1,3,6 isomer are also obtained by a Pd catalyzed dimerization (147–151). The kinetics of thermally induced dimerization to COD has also been studied (152).

One of the butadiene dimerization products, COD, is commercially manufactured and used as an intermediate in a process called FEAST to produce linear α,ω-dienes (153). COD or cyclooctene *[931-87-3]*, obtained from partial hydrogenation, is metathesized with ethylene to produce 1,5-hexadiene *[592-42-7]* or 1,9-decadiene *[1647-16-1]*, respectively. Many variations to make other diolefins have been demonstrated. Huls AG also metathesized cyclooctene with itself to produce an elastomer useful in rubber blending (154). The cyclic *cis,trans,trans*-triene described above can be hydrogenated and oxidized to manufacture dodecanedioic acid *[693-23-2]*. The product was used in the past for the production of the specialty nylon-6,12, Qiana (155,156).

The trimerization to produce *cis,trans,trans*-1,5,9-cyclododecatriene has also been practiced commercially using a Ziegler-Natta catalyst $TiCl_4$–$Al_2(C_2H_5)_3Cl_3$ (154).

Linear dimerization and oligomerization of butadiene can be achieved by using a number of catalyst systems based on Pd, Ni (158–161), and Fe (162). 1,7-Octadiene can be obtained selectively when the dimerization is carried out in the presence of a reducing agent such as formic acid (163–165) or H_2 CO_2 (166).

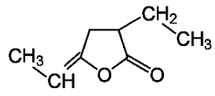


Ziegler-type catalysts based upon Co, Ni, and Fe and in the presence of aluminum alkyls codimerize butadiene with olefins such as ethylene,

producing 1,4-hexadiene derivatives. A rhodium-based catalyst can be used to produce all the *trans*-1,4-hexadiene used as the termonomer in the commercial EPDM (155,156) (see ELASTOMERS, SYNTHETIC, ETHYLENE PROPYLENE DIENE RUBBER). In contrast, cobalt and iron catalysts are known to give the cis-isomer.

Telomerization Reactions. Butadiene can react readily with a number of chain-transfer agents to undergo telomerization reactions. The more often studied reagents are carbon dioxide (167–178), water (179–181), ammonia (182), alcohols (183–185), amines (186), acetic acid (187), water and CO_2 (188), ammonia and CO_2 (189), epoxide and CO_2 (190), mercaptans (191), and other systems (171). These reactions have been widely studied and used in making unsaturated lactones, alcohols, amines, ethers, esters, and many other compounds.

Reaction between butadiene and CO_2 has been extensively studied (171) since the reaction was first demonstrated (167–170). This reaction has been shown to be catalyzed by Pd (172,173), Ni (174), Ru (175), Pt (178), and Rh (172,173) catalysts. Products include gamma (5) and delta lactones (6), acids (7,8), and esters (9). Mechanistic studies have shown that butadiene initially forms a dimer (Pd, Ru, Ni) or trimer (Rh) intermediate followed by CO_2 insertion (171). The fate of these intermediates depends on the metal, the ligands, and the reaction conditions.



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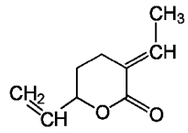

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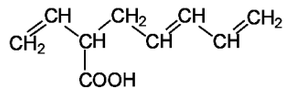

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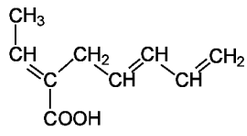

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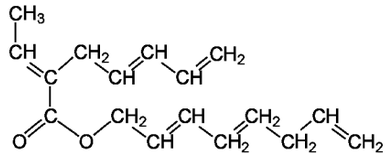


(9)

The delta lactone can be obtained in very high yields when triisopropylphosphine or tricyclohexylphosphine is the ligand along with $Pd(acac)_2$ as the metal source (171).

Coupling of butadiene with CO_2 under electrochemically reducing conditions produces decadienedioic acid, and pentenoic acid, as well as hexenedioic acid (192). A review article on diene telomerization reactions catalyzed by transition metal catalysts has been published (193).

Polymerization Reactions. The polymerization of butadiene with itself and with other monomers represents its largest commercial use. The commercially most important polymers are styrene–butadiene rubber (SBR), polybutadiene (BR), styrene–butadiene latex (SBL), acrylonitrile–butadiene–styrene polymer (ABS), and nitrile rubber (NR). The reaction mechanisms are free-radical, anionic, cationic, or coordinate, depending on the nature of the initiators or catalysts (194–196).

Different grades of SBR copolymers are prepared by either free-radical initiated emulsion polymerization or anionic solution polymerization. The technology was developed during World War II to produce a substitute for natural rubber. The properties of these SBRs are so good that natural rubber has never again regained its importance. Today, SBR represents the single largest use of butadiene (see ELASTOMERS, SYNTHETIC, BUTYL RUBBER).

The original SBR process is carried out at ~50°C and is referred to as hot polymerization. It accounts for only about 5% of all the rubber produced today. The dominant cold polymerization technology today employs more active initiators to effect polymerization at about 5°C. It accounts for about 85% of the products manufactured. Typical emulsion polymerization processes incorporate about 75% butadiene. The initiators are based on persulfate in conjunction with mercaptans (197), or organic hydroperoxide in conjunction with ferrous ion (198). The rest of SBR is produced by anionic solution polymerization. The density of unvulcanized SBR is 0.933 (199). The T_g ranges from −59°C to −64°C (199).

Homopolymerization of butadiene can proceed via 1,2- or 1,4-additions. The 1,4-addition produces the geometrically distinguishable trans or cis structures with internal double bonds on the polymer chains, 1,2-Addition, on the other hand, yields either atactic, isotactic, or syndiotactic polymer structures with pendent vinyl groups (Fig. 2). Commercial production of these polymers started in 1960 in the United States. Firestone and Goodyear account for more than 60% of the current production capacity (see ELASTOMERS, SYNTHETIC POLYBUTADIENE).

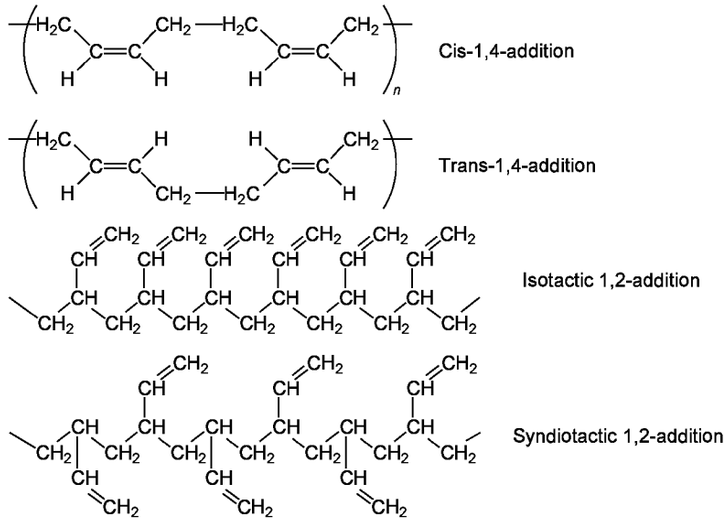


Fig. 2. Modes of addition of butadiene.

Very high *cis*-1,4-addition (~80%) imparts more desirable properties for applications like heavy-duty tires (200). Structural properties of some typical polybutadienes are listed in Table 3 (200–202).

Table 3. Properties of Polybutadiene

Type[a]	Unit cell	Density	Melting point, °C	T_g, °C
1,4-*cis*	monoclinic	1.01	2	106
1,4-*trans*-	hexagonal[b]			107
modification I		0.97	97	
modification II		0.93	145	
1,2-syndiotactic	rhombic	0.96	154	28
1,2-isotactic	rhombohedral	0.96	120	

[a] See Figure 2.
[b] Up to 60°C.

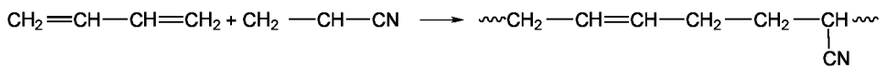
Extensive efforts have been made to develop catalyst systems to control the stereochemistry, addition site, and other properties of the final polymers. Among the most prominant ones are transition metal-based catalysts including Ziegler or Ziegler-Natta type catalysts. The metals most frequently studied are Ti (203,204), Mo (205), Co (206–208), Cr (206–208), Ni (209,210), V (205), Nd (211–215), and other lanthanides (216). Of these, Ti, Co, and Ni complexes have been used commercially. It has long been recognized that by varying the catalyst compositions, the trans cis ratio for 1,4-additions can be controlled quite selectively (204). Catalysts have also been developed to control the ratio of 1,4- to 1,2-additions within the polymers (203).

In situ preparation of polymer blends of 1,4-polybutadiene with polystyrene, or poly(1-butene) has been achieved by using the heterogeneous Ziegler-Natta type catalyst $(C_2H_5)_2AlCl–Ti(OC_4H_9)_4$ in the host polymers (217). Homogeneous catalysts can also be used to catalyze these reactions (218).

Anionic polymerization of butadiene has been intensively investigated over the years. Alkali metals and their alkyl derivatives are most frequently used. The process employing alkyllithium compounds as the initiators was first commercialized in the 1950s. Typical vinyl (1,2-addition) content is about 10–25%, with the balance about evenly divided between *cis*- and *trans*-1,4-addition, depending on the alkyllithium catalyst selected (219). The vinyl content can be increased substantially by the addition of polar compounds such as ethers or amines to the reaction mixture (202,220,221). The most common catalyst used commercially appears to be butyllithium. The products are mostly amorphous and provide desirable vulcanized rubber properties (202). By taking advantage of the living polymer nature of the reaction, products containing various end groups, such as —OH, —COOH, —SH, and others, can be prepared by terminating the polymerization with the proper reagent (195).

Another better studied system is the Alfin (alkoxide–olefin) catalyst, which is composed of a sodium salt, sodium alkoxide, and allylsodium (222). Similarly, there are many different modifications of the system to produce polymers with different 1,2- to 1,4-addition ratios as well as other properties (223).

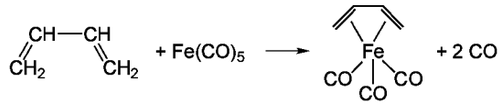
Acrylonitrile–butadiene copolymers (nitrile–butadiene rubber, NBR) are also produced via emulsion polymerization of butadiene with acrylonitrile, CH_2 CH CN*[107-13-1]*.



ABS (acrylonitrile–butadiene-styrene) resins are two-phase blends. These are prepared by emulsion polymerization or suspension grafting polymerization. Products from the former process contain 20–22% butadiene; those from the latter, 12–16%.

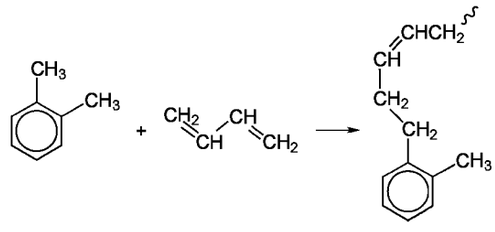
Butadiene can also be copolymerized with a large number of other olefins (224) and SO_2 (225).

Other Reactions. Due to the highly reactive conjugated double bonds, butadiene can undergo many reactions with transition metals to form organometallic complexes. For instance, iron pentacarbonyl reacts with butadiene to produce the tricarbonyl iron complex (10) (226). This and many other organometallic complexes have been covered (227).



(10)

Side-chain anionic alkylation reactions with aromatic compounds take place when catalyzed with strong basic catalysts, like Na–K (228). The yield is 83% when *o*-xylene reacts with butadiene



Manufacturing

The pattern of commercial production of 1,3-butadiene parallels the overall development of the petrochemical industry. Since its discovery via pyrolysis of various organic materials, butadiene has been manufactured from acetylene as well as ethanol, both via butanediols (1,3- and 1,4-) as intermediates (see ACETYLENE DERIVED CHEMICALS). On a global basis, the importance of these processes has decreased substantially because of the increasing production of butadiene from petroleum sources. China and India still convert ethanol to butadiene using the two-step process while Poland and the former USSR use a one-step process (229,230). In the past butadiene also was produced by the dehydrogenation of *n*-butane and oxydehydrogenation of *n*-butenes. However, butadiene is now primarily produced as a by-product in the steam cracking of hydrocarbon streams to produce ethylene. Except under market dislocation situations, butadiene is almost exclusively manufactured by this process in the United States, Western Europe, and Japan.

Steam Cracking. Steam cracking is a complex, highly endothermic pyrolysis reaction. During the reaction a hydrocarbon feedstock is heated to approximately 800°C and 34 kPa (5 psi) for less than a second during which carbon–carbon and carbon–hydrogen bonds are broken. As a result, a mixture of olefins, aromatics, tar, and gases are formed. These products are cooled and separated into specific boiling range cuts of C_1, C_2, C_3, C_4, etc. The C_4 fraction contains butadiene, isobutylene, 1-butene, 2-butene, and some other minor hydrocarbons. The overall yields of butadiene depend on both process parameters (231) and the composition of feedstocks (Table 4) (232). Generally, heavier steam cracking feedstocks produce greater amounts of butadiene as a by-product. Thus, with heavier feedstocks like light naphtha or virgin gas oil, up to about 5.4 wt % of the total product is butadiene. The processes of separating butadiene from the other C_4 compounds are described later.

Table 4. Product Distribution from Steam Cracking Various Feedstocks[a]

	Product yield, wt %					
Feedstock	Ethylene	Propylene	Butadiene	Butenes	BTX	Fuel products
ethane	77.5	2.8	1.9	0.8		17.0
propane	42.0	16.8	3.0	1.3	3.0	33.9
light naphtha	33.7	15.6	4.5	4.2	9.1	32.9
light VGO[b]	20.4	14.1	5.4	6.3	8.5	45.3

[a] Ref. 232.

[b] VGO vacuum gas oil.

Dehydrogenation of *n*-Butane. Dehydrogenation of *n*-butane *[106-97-8]* via the Houdry process is carried out under partial vacuum, 35–75 kPa (5–11 psi), at about 535–650°C with a fixed-bed catalyst. The catalyst consists of aluminum oxide and chromium oxide as the principal components. The reaction is endothermic and the cycle life of the catalyst is about 10 minutes because of coke buildup. Several parallel reactors are needed in the plant to allow for continuous operation with catalyst regeneration. Thermodynamics limits the conversion to about 30–40% and the ultimate yield is 60–65 wt % (233).

Oxydehydrogenation of *n*-Butenes. Normal butenes can be oxidatively dehydrogenated to butadiene in the presence of high concentration of steam with fairly high selectivity (234). The conversion is no longer limited by thermodynamics because of the oxidation of hydrogen to water. Reaction temperature is below about 600°C to minimize over oxidation. Pressure is about 34–103 kPa (5–15 psi).

Separation and Purification. Separation and purification of butadiene from other components is dominated commercially by the extractive distillation process. The most commonly used solvents are acetonitrile and dimethylformamide. Dimethylacetamide, furfural, and *N*-methyl-2-pyrrolidinone also accomplish the separation. These solvents are aprotic polar compounds that have high complexing affinity toward the more polarizable butadiene than other olefins in the streams. Among the many factors that must be considered in choosing the solvent process are cost, solvency, thermal stability, viscosity, toxicity, corrosivity, heat of vaporization, and fouling. The fact that no single solvent has dominated the process suggests that there are no significant differences in both operation and economics using most of these solvents. There are continuous efforts around the world to search for solvents (235,236) that reduce fouling (237,238) and improve operations (239,240). A typical process schematic is shown in Figure 3. Processes using membranes for butadiene separation have also been patented (241,242).

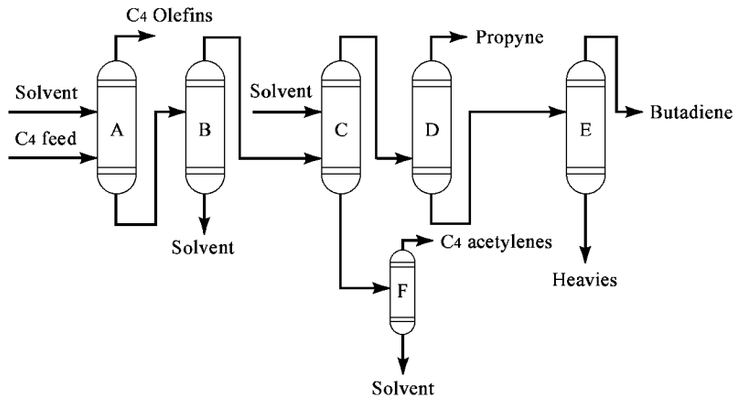


Fig. 3. Separation and purification of butadiene: A, first extraction distillation tower; B, solvent stripper; C, second extraction distillation tower; D, topping tower; E, tailing tower; F, solvent recovery towers.

Another approach to separate butadiene from other hydrocarbons is to use a solution containing cuprous ammonium acetate that forms a weak copper(I) complex with butadiene (243,244). The latter process has been used in a number of plants.

In commercial extraction operations, the C_4 fractions that contain butadiene, isobutene, and 1- and 2-butenes usually first go through a butadiene extraction unit in which the butadiene is removed. This may be followed by isobutylene removal via reaction between isobutylene and methanol to form methyl *t*-butyl ether *[1634-04-4]* (MTBE). The butenes are then distilled from the MTBE. 1-Butene may then be separated from 2-butene by distillation.

Handling, Storage, and Shipping

Large quantities of butadiene are manufactured, stored, transported, and handled in a safe manner every day. Typical product specifications are listed in Table 5. However, butadiene reacts with a large number of chemicals, has an inherent tendency to dimerize and polymerize, and is toxic. Therefore, specific handling, storage, and shipping procedures must be followed. A review of means to prevent occupational exposure during handling, storage, and shipping has been published (245).

Table 5. Butadiene Specifications and Test Methods[a]

Component	Specification	Test method
1,3-butadiene	>99.5%	ASTM D2593
inhibitor[b], wppm	50–150	ASTM D1157
impurities, wppm, max		
1,2-butadiene	20.0	ASTM D2593
propadiene	10.0	ASTM D2593
acetylenes (methyl, ethyl, vinyl)	20.0	ASTM D2593
dimers	500.0	ASTM D2426
isoprene	10.0	ASTM D2593
C5s	500.0	ASTM D2593 or D2426
sulfur	5.0	ASTM D4045 or D2784
peroxides (calculated as H_2O_2)	5.0	ASTM D1022
ammonia	5.0	water wash and ASTM D1426
water	300.0	Karl Fischer or panametric dew point
carbonyls	10.0	ASTM D4423
nonvolatile residues, wt %	0.05	ASTM D1025
oxygen in gas phase, vol %	0.10	teledyne oxygen analyzer

[a] *Courtesy of Exxon Chemical Co.*

[b] *t*-Butylcatechol *[27213-78-1]* TBC.

The thermally induced Diels-Alder dimerization reaction producing vinylcyclohexene is very difficult to prevent except by lowering the storage temperature (246). Since the reaction rate increases about ninefold for every 20°C increase in temperature (Table 6), care must be taken to keep butadiene at a low temperature.

Table 6. Effects of Temperature on Dimerization Rate of Butadiene

Temperature, °C	Butadiene, % dimerized/h
20	0.00015
40	0.0014
60	0.013
80	0.12
100	1.1

Butadiene reacts readily with oxygen to form polymeric peroxides, which are not very soluble in liquid butadiene and tend to settle at the bottom of the container because of their higher density. The peroxides are shock sensitive; therefore it is imperative to exclude any source of oxygen from butadiene. Addition of antioxidants like *t*-butylcatechol (TBC) or butylated hydroxy toluene (BHT) removes free radicals that can cause rapid exothermic polymerizations. Butadiene shipments now routinely contain about 100 ppm TBC. Before use, the inhibitor can easily be removed (247,248). Inert gas, such as nitrogen, can also be used to blanket contained butadiene (249).

Butadiene is also known to form rubbery polymers caused by polymerization initiators like free radicals or oxygen. Addition of antioxidants like TBC and the use of lower storage temperatures can substantially reduce fouling caused by these polymers. Butadiene and other olefins, such as isoprene, styrene, and chloroprene, also form so-called popcorn polymers (250). These popcorn polymers are hard, opaque, and porous. They have been reported to

ignite spontaneously on exposure to air and, therefore, are usually kept under water. They grow faster in the presence of seeds, or oxygen and rust. Because popcorn polymers can grow exponentially (251), they can generate tremendous pressure resulting in sudden rupture or plugging of containers, distillation towers, and pipes (252). It is reported that rigorous exclusion of oxygen from the system, metal surface passivation, and removal of popcorn polymer seeds can mitigate most of this problem (251). Addition of antioxidants will also help, but the high boiling points of many of these materials render them effective primarily in the liquid phase. Recently, a comprehensive study of this phenomenon and effective mitigation methods have been investigated, developed, and are available for license (253).

Butadiene is primarily shipped in pressurized containers via railroads or tankers. U.S. shipments of butadiene, which is classified as a flammable compressed gas, are regulated by the Department of Transportation (254). Most other countries have adopted their own regulations (30). Other information on the handling of butadiene is also available (255). As a result of the extensive emphasis on proper and timely responses to chemical spills, a comprehensive handbook from the National Fire Protection Association is available (256).

Health, Safety, and Toxicology

Butadiene has been used widely in producing many important industrial polymers and other products. Thus over the years the effects on plant workers who have been exposed to different levels of butadiene have been under increasing scrutiny from manufacturers, users, health organizations, as well as government agencies. Short-term exposure to high concentrations of butadiene may cause irritation to the eyes, nose, and throat. Dermatitis and frostbite may result from exposure to the liquid and the evaporating gas (245). Long-term physiological reactions to 1,3-butadiene may vary individually.

Exposure studies have been made using mice and rats (257). These experiments have demonstrated species differences in butadiene toxicity and carcinogenicity. Butadiene was found to be a potent carcinogen in the mouse, but only a weak carcinogen in the rat. The interpretations have focused on differences in toxification rates and detoxification metabolisms as causative factors (257). The metabolism is believed to proceed through intermediates involving butadiene monoepoxide and butadiene diepoxide (257). A similar mechanism has been proposed for its biodegradation pathway (258).

A retrospective epidemiological study covering a period of 36 years and a population of approximately 14,000 workers from eight SBR production facilities in the United States and Canada was the largest of several such studies conducted (257–259). The study covered the period between 1943 and 1976 with an update from 1977 to 1985. Despite the difficulty in ascertaining the exposure levels, the authors of that paper suggested there were no statistically significant differences in tumor mortality in total or for any specific cause of death as compared to the general population (257). In several epidemiological studies elevation in mortality were observed for small subgroups and tumor types. Interpretation of these findings is still incomplete (260,261). Based on the assessment of these studies, the American Conference of Governmental Industrial Hygienists (ACGIH) adopted a TLV of 10 ppm for 1,3-butadiene in 1982. Subsequently, in 1989 OSHA proposed a 10-ppm 15-min exposure level and a 2-ppm TLV (Table 7).

Table 7. Exposure Limits of Butadiene in Selected Countries

Country	Exposure limit[a]
Belgium	10 ppm
Germany	5 ppm before polymerization
	15 ppm after polymerization
Italy	10 ppm (predicted)
Japan	10 ppm (voluntary adoption)
Latin America	1 ppm (predicted)
the Netherlands	50 ppm
United Kingdom	10 ppm
United States	10 ppm (ACGIH, 1982)
	10 ppm for 15 min (OSHA 1990)[b]
	2 ppm 8-h time weighted average (OSHA, 1990)[b]

[a] Ref. 262 unless otherwise noted.
[b] Ref. 263.

There have been many reviews published on the toxicity of butadiene (264). A summary of environmental health perspectives was presented at the 1988 Symposium on Toxicology, Carcinogenesis, and Human Health Effects of 1,3-Butadiene (265). Detailed comparisons of various personal monitoring devices are available (266), and control of occupational exposure to 1,3-butadiene has been reviewed (267).

Uses and Economics

Butadiene is used primarily in polymers, including SBR, BR, ABS, SBL, and NR. In 1989 these uses accounted for about 79% of butadiene consumed in the United States (268,269). Styrene–butadiene rubber, the single largest user of butadiene, consumes about 540,000 kg of butadiene, or 32% of the total. It is followed by polybutadiene rubber at 23%. Consumption for the other polymers, ABS, styrene–butadiene latex, polychloroprene, and nitrile rubber are listed in Table 8.

Table 8. Pattern of Butadiene Uses in the United States, 1989[a]

End use	Percentage of total, %
synthetic elastomers	63.3
styrene–butadiene rubber (SBR)	32.0
polybutadiene (BR)	23.0
polychloroprene (Neoprene)	5.6
nitrile rubber (NR)	2.7
polymers and resins	15.7
acrylonitrile–butadiene–styrene (ABS)	4.7
styrene–butadiene copolymer (latex)	11.0
chemicals and other uses	21.0
adiponitrile	13.0
others	8.0

[a] *Courtesy of Exxon Chemical Co.*

Another significant butadiene use is for manufacturing adiponitrile, $NC(CH_2)_4CN$ *[111-69-3]*, a precursor for nylon-6,6 production. It accounted for about 13% of total U.S. butadiene consumption in 1989. Other miscellaneous chemical uses, such as for ENB (ethylidene norbornene) production, account

for 8% combined (Fig. 4) (268).

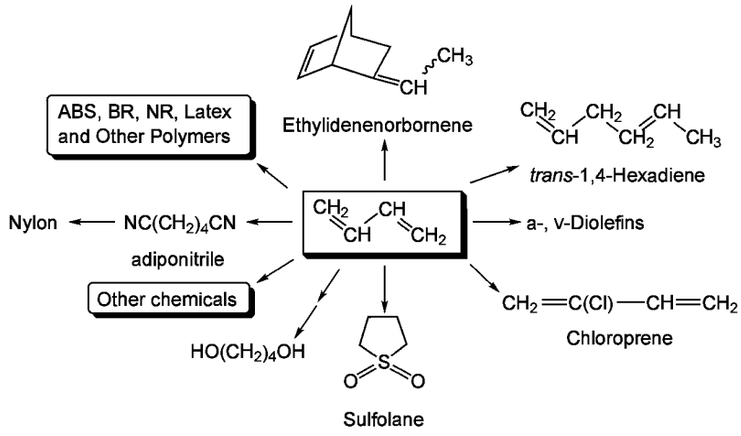


Fig. 4. Commercial uses of butadiene.

Since the bulk of butadiene is recovered from steam crackers, its economics is very sensitive to the selection of feedstocks, operating conditions, and demand patterns. Butadiene supply and, ultimately, its price are strongly influenced by the demand for ethylene, the primary product from steam cracking. Currently there is a worldwide surplus of butadiene. Announcements of a number of new ethylene plants will likely result in additional butadiene production, more than enough to meet worldwide demand for polymers and other chemicals. When butadiene is in excess supply, ethylene manufacturers can recycle the butadiene as a feedstock for ethylene manufacture.

During the 1980s, the list price of butadiene varied between about $0.20 kg and $0.88 kg. Since the largest use for butadiene is in tire manufacturing, its demand is strongly influenced by the fortunes of the auto industry and the trend to longer lasting tires. It is shipped around the world (270). Table 9 summarizes the global production and trading patterns for 1989 (268).

Table 9. Global Butadiene Consumption and Distribution[a], 1989, 10^3 t

	Production	Import	Export
North America	1520	300	79
South America	262	100	20
Western Europe	1868		454
Eastern Europe	1492	102	50
Africa and Middle East	150	60	
Asia and the Pacific	1327	137	75

[a] *Courtesy of Exxon Chemical Co.*

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BUTANEDIOLS.

See GLYCOLS.

BUTANES.

See HYDROCARBONS, C_1–C .

BUTENE POLYMERS.

See OLEFIN POLYMERS.

BUTTER.

See MILK AND MILK PRODUCTS.

BUTYL ACETATE.

See ESTERS, ORGANIC.

BUTYL ALCOHOLS

Butyl alcohols encompass the four structurally isomeric 4-carbon alcohols of empirical formula $C_4H_{10}O$. One of these, 2-butanol, can exist in either the optically active *R*( ) or *S*( ) configuration or as a racemic ( ) mixture *[15892-23-6]*.

Physical and Chemical Properties

The butanols are all colorless, clear liquids at room temperature and atmospheric pressure with the exception of *t*-butyl alcohol which is a low melting solid (mp 25.82°C); it also has a substantially higher water miscibility than the other three alcohols. Physical constants (1) of the four butyl alcohols are given in Table 1.

Table 1. Physical Properties of the Butyl Alcohols (Butanols)

Common Name CAS Registry Number	*n*-Butyl alcohol *[71-36-3]*	Isobutyl alcohol *[78-83-1]*	*sec*-Butyl alcohol *[78-92-2]*	*t*-Butyl alcohol *[75-65-0]*
systematic name	1-butanol	2-methyl-1-propanol	2-butanol	2-methyl-2-propanol
formula	$CH_3(CH_2)_3OH$	$(CH_3)_2CHCH_2OH$	$CH_3CH(OH)C_2H_5$	$(CH_3)_3COH$
critical temperature, °C	289.90	274.63	262.90	233.06
critical pressure, kPa[a]	4423	4300	4179	3973
critical specific volume, m^3 kg mol	0.275	0.273	0.269	0.275
normal boiling point, °C	117.66	107.66	99.55	82.42
melting point, °C	89.3	108.0	114.7	25.82
ideal gas heat of formation at 25°C, kJ mol[b]	274.6	283.2	292.9	312.4
heat of fusion, kJ mol[b]	9.372	6.322	5.971	6.703
heat of vaporization at normal boiling point, kJ g[b]	43.29	41.83	40.75	39.07
liquid density, kg m^3 at 25°C	809.7	801.6	806.9	786.6[c]
liquid heat capacity at 25°C, kJ (mol·K)[b]	0.17706	0.18115	0.19689	0.2198 at mp
refractive index at 25°C	1.3971	1.3938	1.3949	1.3852
flash point, closed cup, °C	28.85	27.85	23.85	11.11
dielectric constant, ε	17.5^{25}	17.93^{25}	16.56^{20}	12.47^{30}
dipole moment × 10^{30}, C·m[d]	5.54	5.47	5.54	5.57

solubility parameter, $(MJ\ m^{3})^{0.5}$ [e] at 25°C	23.354	22.909	22.541	21.603
solubility in water at 30°C, % by weight	7.85	8.58	19.41	miscible
solubility of water in alcohol at 30°C, % by weight	20.06	16.36	36.19	miscible

[a] To convert kPa to mm Hg, multiply by 7.50.

[b] To convert kJ to kcal, divide by 4.184.

[c] For the subcooled liquid below melting point.

[d] To convert C·m to debyes, divide by 3.336×10^{-30}.

[e] To convert $(MJ\ m^{3})^{0.5}$ to $(cal\ cc)^{0.5}$, multiply by $0.239^{0.5}$.

Physical constants (2) for the optically pure stereoisomers of 2-butanol have been reported as follows:

	CAS Registry Number	d_4^{20}	n_D^{20}	$[\alpha]_D^{27}$
(*S*)-(+)-2-butanol	*[4221-99-2]*	0.8025^{27}	1.3954	+13.52
(*R*)-(-)-2-butanol	*[14898-79-4]*	0.8042^{25}	1.3970	13.52

The most common azeotropes (3,4) formed by the butanols are given in Table 2. Butyl alcohol liquid vapor pressure temperature responses (5,6), which are important parameters in direct solvent applications, are presented in Figure 1. Similarly, viscosity temperature plots (1) for the four butanols are presented in Figure 2.

Table 2. Azeotropic Mixtures of the Butyl Alcohols

Components	Weight %	Boiling point of mixture, °C
	Binary azeotropes	
1-butanol		
water	42.4	92.6
n-butyl acetate	32.8	117.6
n-butyl formate	76.3	105.8
methyl isovalerate	67	113
cyclohexane	90	79.8
tetrachloroethylene	68	110.0
ethyl isobutyrate	83	109.2
toluene	68	105.5
isobutyl alcohol		
water	33	90
cyclohexane	86	78.1
benzene	91	79.8
toluene	56	101.1
2-butanol		
water	32	88.5
2-butyl acetate	13.7	99.6
	Ternary azeotropes	
1-butanol	10	83.6
n-butyl formate	68.7	
water	21.3	
1-butanol	27.4	89.4
n-butyl acetate	35.3	
water	37.3	

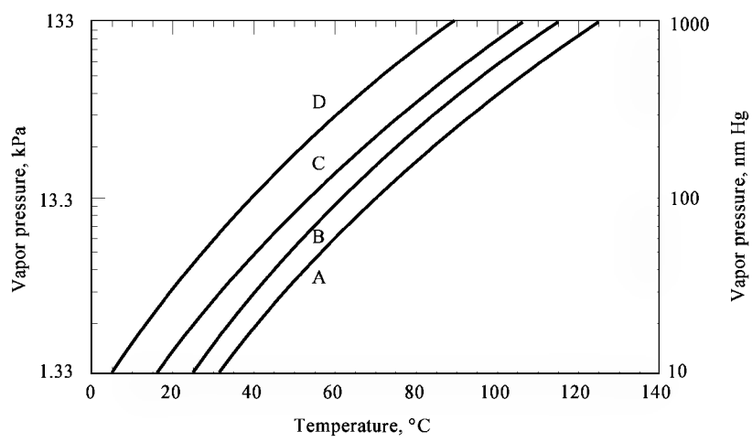


Fig. 1. Vapor pressure of butyl alcohols: A, *n*-butyl; B, isobutyl; C, *sec*-butyl; D, *t*-butyl. To convert kPa to mm Hg, multiply by 7.5.

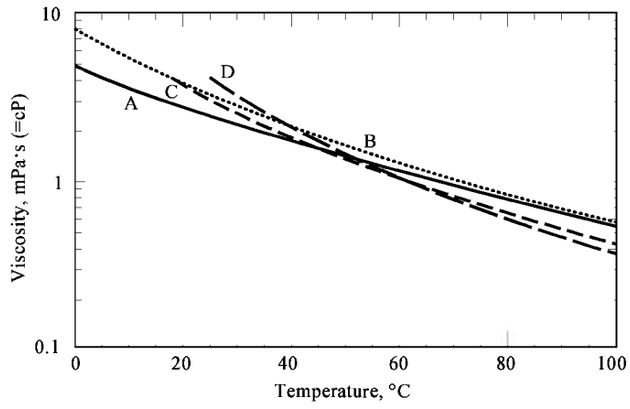


Fig. 2. Liquid viscosity of butyl alcohols: A, 1-butanol; B, isobutyl alcohol; C, 2-butanol; D, *t*-butyl alcohol.

The butanols undergo the typical reactions of the simple lower chain aliphatic alcohols. For example, passing the alcohols over various dehydration catalysts at elevated temperatures yields the corresponding butenes. The ease of dehydration increases from primary to tertiary alcohol: *t*-butyl alcohol undergoes dehydration with dilute sulfuric acid at low temperatures in the liquid phase whereas the other butanols require substantially more stringent conditions.

With the exception of the *t*-butyl compound, the butyl alcohols are dehydrogenated to the corresponding carbonyl compounds when passed over copper or silver catalysts at temperatures around 300°C. Thus, *n*- and isobutyl alcohols are dehydrogenated to *n*- and isobutyraldehyde, respectively, while 2-butanol gives methyl ethyl ketone (2-butanone). Continued or more vigorous oxidation of *n*- and isobutyl alcohol yield the corresponding carboxylic acids whereas 2-butanol is degraded to acids of shorter chain length.

The butyl alcohols undergo esterification with organic acids in the usual manner in the presence of trace amounts of mineral acid catalysts. Esterification is fastest with *t*-butyl alcohol and slowest with the primary alcohols although *t*-butyl alcohol undergoes substantial dehydration in the presence of the typical acid esterification catalysts.

1-Butanol and isobutyl alcohol are aminated with ammonia over alumina at 300–350°C to give the corresponding mono-, di-, and tributylamines.

Manufacture

The principal commercial source of 1-butanol is *n*-butyraldehyde *[123-72-8]*, obtained from the Oxo reaction of propylene. A mixture of *n*- and isobutyraldehyde *[78-84-2]* is obtained in this process; this mixture is either separated initially and the individual aldehyde isomers hydrogenated, or the mixture of isomeric aldehydes is hydrogenated directly and the *n*- and isobutyl alcohol product mix separated by distillation. Typically, the hydrogenation is carried out in the vapor phase over a heterogeneous catalyst. For example, passing a mixture of *n*- and isobutyraldehyde with 60:40 H_2:N_2 over a CuO–ZnO–NiO catalyst at 25–196°C and 0.7 MPa proceeds in 99.95% efficiency to the corresponding alcohols at 98.6% conversion (7,8) (see BUTYRALDEHYDES; OXO PROCESS).

In a process which is now largely of historical interest, 1-butanol has been produced from ethanol *[64-17-5]* via successive dehydrogenation (to acetaldehyde *[75-07-0]*), condensation (to crotonaldehyde *[4170-30-3]*) and hydrogenation.

$$CH_3CH_2OH \rightarrow CH_3CHO \rightarrow CH_3CH{=}CHCHO \rightarrow CH_3CH_2CH_2CH_2OH$$

Alternatively, the intermediate acetaldehyde (qv) for this process was obtained from ethylene by the Wacker process (9). A small amount of *n*-butyl alcohol is produced in the United States by the Ziegler-Natta chain growth reaction from ethylene *[74-85-1]* (10).

The earliest commercial process to 1-butanol, still practiced extensively in many Third World countries, employs fermentation of molasses or corn products with *Clostridium acetobutylicum* (11–13). Acetone and ethanol are obtained as coproducts.

A fermentation route to 1-butanol based on carbon monoxide employing the anaerobic bacterium, *Butyribacterium methylotrophicum* has been reported (14,15). In contrast to other commercial catalytic processes for converting synthesis gas to alcohols, the new process is insensitive to sulfur contaminants. Current productivities to butanol are 1 g L, about 10% of that required for commercial viability. Researchers hope to learn enough about the bacteria's control mechanisms to be able to use recombinant DNA to make the cells produce more butanol.

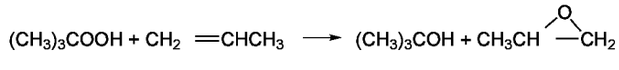
As of January 1, 1990, the total U.S. capacity of 1-butanol was 591,000 t per year. Capacity for an additional 545,000 t per year of *n*-butyl alcohol is operated in Western Europe and Southeast Asia (10).

Commercial isobutyl alcohol is made almost exclusively from the hydrogenation of isobutyraldehyde obtained by the hydroformylation of propylene. However, this alcohol is also commonly obtained as a coproduct in the Fischer Tropsch synthesis of methanol (16,17).

2-Butanol is produced commercially by the indirect hydration of *n*-butenes. However, current trends are towards the employment of inexpensive Raffinate II type feedstocks, ie, C-4 refinery streams containing predominantly *n*-butenes and saturated C-4s after removal of butadiene and isobutylene. In the traditional indirect hydration process, *n*-butenes are esterified with liquid sulfuric acid and the intermediate butyl sulfate esters hydrolyzed. DEA Mineraloel (formerly Deutsche Texaco) currently operates a 2-butanol plant employing a direct hydration of *n*-butenes route (18) with their own proprietary catalyst.

The Arco Propylene Oxide Process produces *t*-butyl alcohol as a coproduct of propylene oxide *[75-56-9]* when isobutane is used as a starting material.

$$(CH_3)_3CH + O_2 \rightarrow (CH_3)_3COOH$$



The process can be modified to give predominantly or solely *t*-butyl alcohol. Thus, *t*-butyl hydroperoxide (and *t*-butyl alcohol) produced by oxidation of isobutane in the first step of the process can be decomposed under controlled, catalytic conditions to give gasoline grade *t*-butyl alcohol (GTBA) in high selectivity (19–22).

$$(CH_3)_3COOH \xrightarrow{\text{Mo catalyst}} (CH_3)_3COH + \tfrac{1}{2}O_2$$

The oxygen released is recycled to the isobutane oxidation step. GTBA contains some methanol and acetone coproducts and is used as a blending agent for gasoline.

The other significant industrial route to *t*-butyl alcohol is the acid catalyzed hydration of isobutylene (24), a process no longer practiced in the United States. Raffinate I, C-4 refinery streams containing isobutylene *[115-11-7]*, *n*-butenes and saturated C-4s or C-4 fluid catalytic cracker (FCC) feedstocks (23)

may be employed.

Uses

The largest volume commercial derivatives of 1-butanol are *n*-butyl acrylate *[141-32-2]* and methacrylate *[97-88-1]* (10). These are used principally in emulsion polymers for latex paints, in textile applications and in impact modifiers for rigid poly(vinyl chloride). The consumption of *n*-butanol in the United States for acrylate and methacrylate esters is expected to rise to 182,000–186,000 t by 1993 (10).

Butyl glycol ethers, the largest volume derivatives of *n*-butyl alcohol used in solvent applications (10), are obtained from the reaction of 1-butanol with ethylene oxide. The most important of these derivatives, 2-butoxyethanol, is used principally in vinyl and acrylic paints as well as in lacquers and varnishes. It is also employed in aqueous cleaners to solubilize organic surfactants. 2-Butoxyethanol *[111-76-2]* has achieved some growth at the expense of the lower alkoxyethanols (ie, methoxy and ethoxyethanol) because of 2-butoxyethanol's lower toxicity.

1-Butanol is used as a direct solvent in paints and other surface coatings. It acts synergistically with butyl acetate as a latent solvent system for nitrocellulose lacquers and thinners to give a solvent system stronger than either solvent alone. Other direct solvent applications for *n*-butyl alcohol are in the formulation of pharmaceuticals, waxes, and resins.

Butyl acetate *[123-86-4]*, one of the more important derivatives of *n*-butyl alcohol produced commercially, is employed as a solvent in rapid drying paints and coatings. In some instances, butyl acetate, $C_{12}H_{12}O_2$, has replaced ethoxyethyl acetate *[111-15-9]* due to the latter's reported toxicity and teratogenicity. Butyl acetate is used in leather treatment, perfumes, and as a process or reaction solvent and is also used extensively with wood coatings, maintenance coatings, and in coatings for containers and closures.

Additional commercial markets for 1-butanol include plasticizer esters (eg, dibutyl phthalate), butylated melamine–formaldehyde resins, and mono-, di-, and tributylamines.

Historically, isobutyl alcohol was an unwanted by-product of the propylene Oxo reaction. Indeed, isobutyraldehyde the precursor of isobutyl alcohol was occasionally burned for fuel. However, more recently isobutyl alcohol has replaced *n*-butyl alcohol in some applications where the branched alcohol appears to have preferred properties and structure. However, supplies of isobutyl alcohol have declined relative to overall C-4 alcohols, especially in Europe, with the conversion of many Oxo plants to rhodium based processes which give higher normal to isobutyraldehyde isomer ratios. Further the supply of isobutyl alcohol at any given time can fluctuate greatly, since it is the lowest valued derivative of isobutyraldehyde, after neopentyl glycol, methyl isoamyl ketone and certain condensation products (10).

The principal industrial application for isobutyl alcohol is as a direct solvent replacement for 1-butanol. It is also used as a process solvent in the flavor and fragrance, pharmaceutical, and pesticide industries. The maximum employment of isobutyl alcohol was in the mid-1980s when it had a distinct price advantage over 1-butanol (10). More recently, however, with increased demand for other value added derivatives of isobutyraldehyde, the price differential between isobutyl and *n*-butyl alcohols has diminished resulting in a switching back by some consumers to 1-butanol.

Some commercially important isobutyl derivatives include isobutyl acetate, employed as a replacement solvent for *n*-butyl acetate; zinc dialkyldithiophosphate (ZDPP) lube oil additives; isobutyl acrylate *[106-62-8]* and methacrylate *[97-86-9]* monomers; isobutylamines; and amino resins (qv).

Some efforts were made in the early 1980s to employ isobutyl and *n*-butyl alcohols as octane extenders in gasoline. American Methyl Corporation in 1983, under a special waiver of the 1977 Clean Air Act (24), marketed a gasoline blend called Petrocoal containing methanol and a C-4 alcohol which was principally isobutyl alcohol. About 10,000 t of isobutyl and 5000 t of *n*-butyl alcohol were consumed in this application (10). In 1984, the EPA attempted to rescind this waiver and demand for isobutyl alcohol as a gasoline additive dropped to 136.3 t (10). Ultimately, the waiver was rescinded and no isobutyl or *n*-butyl alcohol has been marketed for gasoline additive end use since 1984.

The employment of *t*-butyl alcohol as a gasoline additive in the United States was legitimized through an EPA waiver in 1979 (25), even though *t*-butyl alcohol had been added to gasoline as far back as 1969. Oxinol 50, a gasoline blending component marketed by Arco through the late 1970s, consisted of a 1:1 mixture of methanol and *t*-butyl alcohol which was added to gasoline to 5% by volume (25). Oxinol 50 is no longer marketed in the United States because of concerns about long term engine effects of methanol in gasoline. GTBA, however, is still used extensively in Europe.

t-Butyl alcohol, obtained from hydration of Raffinate I, can be dehydrated and subsequently refined to high purity, polymer-grade isobutylene (25). Alternatively, the isobutylene from alcohol dehydration can react with methanol in the presence of an acid catalyst to give methyl *t*-butyl ether (MTBE) gasoline additive (see ETHERS ORGANIC).

t-Butyl alcohol is employed as a feedstock in Japan to make methyl methacrylate monomer. In one such process (26), the alcohol is oxidized (in two steps) to acrylic acid, which is then esterified with methanol. In a similar process (27), *t*-butyl alcohol is oxidized in the presence of ammonia to give methacrylonitrile *[126-98-7]*. The latter is hydrolyzed to methacrylamide *[79-39-0]* which then reacts with methanol to yield methyl methacrylate *[80-62-6]*.

The glycol ethers obtained from *t*-butyl alcohol and propylene oxide, eg, 1-*t*-butoxy-2-propanol, have lower toxicities than the widely employed 2-butoxyethanol and are used in industrial coatings and to solubilize organic components in aqueous formulations (28).

2-Butanol is employed almost exclusively to make the solvent methyl ethyl ketone *[78-93-3]*.

Quality Specifications and Analysis

With the exception of gasoline grade *t*-butyl alcohol (GTBA), the butanols are generally marketed in bulk in the pure isomeric form. ASTM specifications (29) for *n*-, iso- and *sec*-butyl alcohol are given in Table 3. Butanol specification purity is routinely obtained by gas chromatography (30).

Table 3. ASTM Specification for Butyl Alcohols

ASTM standard	*n*-Butyl D 304-85	Isobutyl D 1719-86	*sec*-Butyl D 1007-85	Specification method
apparent specific gravity				
20 20°C	0.810–0.813	0.802–0.804	0.809–0.809	D268
25 25°C	0.807–0.810	0.794–0.801	0.804–0.806	
color (Pt–Co), max	10	10	10	D1209
distribution range,[a] °C	117 ± 1.7	107.9 ± 2	98–101	D1078
nonvolatile material, mg 100 mL, max	5	5	5	D1353
water, wt % max	0.1	0.2	0.5	D1364 and 1476
acidity, as acetic acid, wt % max	0.005	0.003	0.002	D1613

[a] At 101.3 kPa 760 mm Hg.

A cosmetics industry specification for *t*-butyl alcohol (31) is 99.5% alcohol, a maximum 0.002% acidity (as acetic acid), a maximum of 0.1% water, and a maximum of 0.001% nonvolatile matter.

Health, Safety, and Environmental Considerations

All four butanols are thought to have a generally low order of human toxicity (32). However, large dosages of the butanols generally serve as central nervous system depressants and mucous membrane irritants. Animal toxicity and irritancy data (32) are given in Table 4.

Table 4. . Animal Toxicity and Irritancy Data for Butanols

	LD_{50} rats, mg/kg, oral	LD_{50} rabbits, g/kg, intravenous	Inhalation	Eye injury to rabbits
1-butanol	4.36	5.3	8,000 ppm for 4 h (all rats survived)	5 µL (severe corneal damage)
isobutyl alcohol	3.4	0.6	10,600 ppm for 6 h (all mice survived)	one drop caused moderate to severe irritation
2-butanol	6.5	0.8	16,000 ppm for 4 h (5 of 6 rats died)	severe corneal injury (rabbit)
t-butyl alcohol	3.6	1.5 (mouse)		

The reported odor threshold limits (33) for *n*-, iso, *sec*- and *t*-butyl alcohol are 0.83, 1.6, 2.6, and 47 ppm, respectively.

Flammability characteristics (1) of the four butanols are given in Table 5.

Table 5. Flammability Characteristics of the Butanols

	Flash point, °C	Autoignition temperature, °C	Explosive limits, vol %	
			lower	upper
n-butyl	2–3	342.85	1.4	11.2
isobutyl	28	426.85	1.7	10.9
sec-butyl	21	405.85	1.7	9.8
t-butyl	11	477.85	2.4	8.0

All four butanols are registered in the United States on the Environmental Protection Agency Toxic Substances Control Act (TSCA) Inventory, a prerequisite for the manufacture or importation for commercial sale of any chemical substance or mixture in quantities greater than a 1000 pounds (454 kg). Additionally, the manufacture and distribution of the butanols in the United States are regulated under the Superfund Amendments and Reauthorization Act (SARA), Section 313, which requires that anyone handling at least 10,000 pounds (4545 kg) a year of a chemical substance report to both the EPA and the state any release of that substance to the environment.

Storage and Handling

The C-4 alcohols are preferably stored in baked phenolic-lined steel tanks. However, plain steel tanks can also be employed provided a fine porosity filler is installed to remove any contaminating rust (34).

Storage under dry nitrogen is also recommended since it limits flammability hazards as well as minimizing water pickup. There is a report of an explosion occurring during distillation of a sample of aged 2-butanol (35), suggesting that dangerous levels of peroxides can form in 2-butanol on storage in air.

Piping and pumps used for transfer of the butanols can be made of the same metal as tanks. Centrifugal pumps with explosion-proof electric motor drives are recommended (34).

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BUTYLENES

Butylenes are C_4H_8 mono-olefin isomers: 1-butene, *cis*-2-butene, *trans*-2-butene, and isobutylene (2-methylpropene). These isomers are usually coproduced as a mixture and are commonly referred to as the C_4 fraction. These C_4 fractions are usually obtained as by-products from petroleum refinery and petrochemical complexes that crack petroleum fractions and natural gas liquids. Since the C_4 fractions almost always contain butanes, it is also known as the B–B stream. The linear isomers are referred to as butenes.

Physical Properties

For any industrial process involving vapors and liquids, the most important physical property is the vapor pressure. Table 1 presents values for the constants for a vapor-pressure equation and the temperature range over which the equation is valid for each butylene.

$$\ln P = A + B/T + C*\ln T + D*T**N$$
$$P \text{ is in Pa and } T \text{ is in K} \tag{1}$$

where P is in Pa and T is in KA screening technique (1) was used to select the experimental data (2) used in the regressions. Large deviations often occur at low temperatures because of the inability of the equation to model the data over the entire temperature range accurately. In order to ensure that the equations are of practical value, the regressions are performed so that emphasis is placed on conditions of industrial importance; ie, data at subatmospheric conditions are weighed much less than those at pressures exceeding 101.3 kPa (1 atm).

Table 1. Vapor-Pressure Equation Constants for the Butanes, Butylenes, and Butadienes[a]

	A	B	C	D	N	Temperature range, K
n-butane	61.5623	4259.90	6.20315	3.07575×10^{-7}	2.5	135–423
isobutane	66.7163	4237.62	7.08156	4.00506×10^{-7}	2.5	129–408
1-butene	78.8760	4713.65	9.05743	1.28654×10^{-5}	2.0	126–416
cis-2-butene	71.9534	4681.34	7.87527	1.00237×10^{-5}	2.0	203–358
trans-2-butene	74.3950	4648.45	8.33977	1.20897×10^{-5}	2.0	195–358
isobutylene	83.8683	4822.95	9.90214	1.51060×10^{-5}	2.0	194–359
1,2-butadiene	49.5031	4021.95	4.28893	5.13547×10^{-6}	2.0	200–284
1,3-butadiene	73.0016	4547.77	8.11105	1.14037×10^{-5}	2.0	164–425

[a] See equation 1.

Figure 1 presents the ratio of the vapor pressure of a compound to the vapor pressure of *n*-butane at the same temperature. For the chemically similar species included in this figure, this ratio is a first approximation of the relative volatility of the compound to *n*-butane. Whenever the ratios of two compounds approach one another, it becomes increasingly difficult to separate the compounds by simple distillation. Since the butylenes are usually present in mixtures containing the butanes, the butylenes, and the butadienes, Figure 1 shows the ratios for all these species. Figure 1 implies that separating either isobutylene, 1-butene and 1,3-butadiene, or *n*-butane, *trans*-2-butene and *cis*-2-butene, by conventional distillation would be very difficult, if not impossible. In fact, some binary mixtures containing these components form homogeneous azeotropes. The difficulty of these separations greatly influences the design of all industrial processes involving these compounds. If it is necessary to isolate one of these species from the others, it can be expected that the separation process will be expensive.

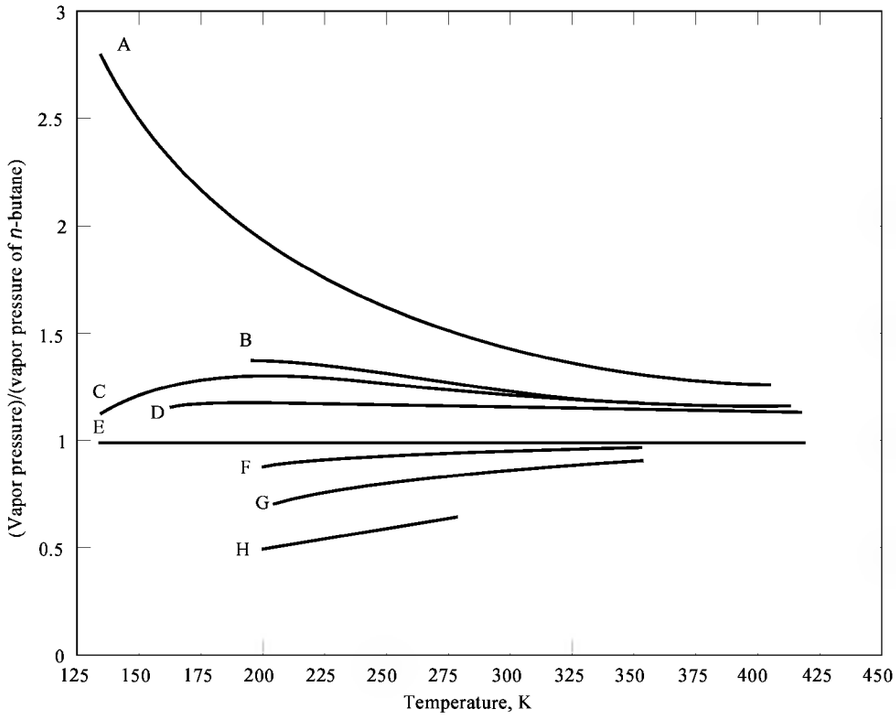


Fig. 1. Vapor-pressure ratios of the C_4 alkanes, alkenes, and dienes with respect to *n*-butane: A, isobutane; B, isobutylene; C, 1-butene; D, 1,3-butadiene; E, *n*-butane; F, *trans*-2-butene, G, *cis*-2-butene; and H, 1,2-butadiene.

Table 2 presents other important physical properties for the butylenes (3). Thermodynamic and transport properties can also be obtained from other sources (4).

Table 2. Physical Properties of the Butylenes

	Values			
Property	1-Butene	*cis*-2-Butene	*trans*-2-Butene	Isobutylene
CAS Registry Number	*[106-98-9]*	*[590-18-1]*	*[624-64-6]*	*[115-11-7]*
molecular weight	56.11	56.11	56.11	56.11
melting point, K	87.80	134.23	167.62	132.79
boiling point, K	266.89	276.87	274.03	266.25
critical temperature, K	419.60	435.58	428.63	417.91
critical pressure, MPa[a]	4.023	4.205	4.104	4.000
critical volume, L mol	0.240	0.234	0.238	0.239
critical compressibility factor	0.277	0.272	0.274	0.275
acentric factor	0.1914	0.2018	0.2186	0.1984
	Ideal gas properties[b] at 298.15 K			
H_f, kJ mol	0.126	6.99	11.18	16.91
G_f, kJ mol	71.34	65.90	63.01	58.11
C_p, J mol·K	85.8	79.4	88.3	90.2
H_{vap}, kJ mol	20.31	22.17	21.37	20.27
H_{comb}, kJ mol	2719	2712	2708	2724
	Saturated vapor at 298.15 K			
viscosity, mPa·s (= cP)	0.00776	0.00782	0.00763	0.00816
thermal conductivity, W (m·K)	0.0151	0.0135	0.0144	0.0158
	Saturated liquid			
density at 298.15 K, mol L	10.47	11.00	10.69	10.49
surface tension at 298.15 K, mN m (= dyn cm)	0.0121	0.0140	0.0132	0.0117
C_p at 266 K, J (mol·K)[b]	121.6	118.8	121.8	123.3
viscosity at 266 K, mPa·s (cP)	0.186	0.214	0.214	0.228
thermal conductivity at 266 K, W (m·K)	0.120	0.124	0.121	0.117
	Flammability limits, vol % in air			
lower limit	1.6	1.6	1.8	1.8
upper limit	9.3	9.7	9.7	8.8
autoignition temperature, K	657	598	597	738

[a] To convert MPa to atm, multiply by 9.869.

[b] To convert kJ to kcal, divide by 4.184.

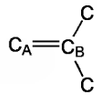
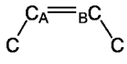
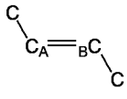
Chemical Properties

The carbon–carbon double bond is the distinguishing feature of the butylenes and as such, controls their chemistry. This bond is formed by sp^2 orbitals (a sigma bond and a weaker pi bond). The two carbon atoms plus the four atoms in the alpha positions therefore lie in a plane. The pi bond which lies over the plane of the atoms acts as a source of electrons in addition reactions at the double bond. The carbon–carbon bond, acting as a substitute, affects the reactivity of the carbon atoms at the alpha positions through the formation of the allylic resonance structure. This structure can stabilize both positive and

negative charges. Thus allylic carbons are more reactive to substitution and addition reactions than alkane carbons (5). Therefore, reactions of butylenes can be divided into two broad categories: (*1*) those that take place at the double bond itself, destroying the double bond; and (*2*) those that take place at alpha carbons.

Differences in reactivity of the double bond among the four isomers are controlled by substitution pattern and geometry. Inductive effects imply that the carbons labeled B in Table 3 should have less electron density than the A carbons. ^{13}C nmr shift data, a measure of electron density, confirm this.

Table 3. ^{13}C Nmr Shifts and Hydration Activation Energies for Butylenes

Butylene	^{13}C Nmr[a] ppm shift at		E_a for hydration, kJ mol[b] at	
	A	B	A	B
$C_A—C_B—C—C$	80.4	53.5	188	145
	82.0[c]	50.4[c]	711	108
	69.1	69.1	203	203
	67.7	67.7	203	203

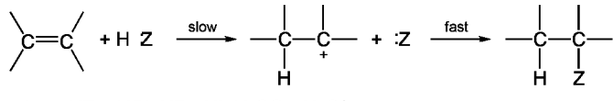
[a] Relative to external CS_2 reference.

[b] To convert kJ to kcal, divide by 4.184.

[c] These values obtained by interpolation.

The electron-rich carbon–carbon double bond reacts with reagents that are deficient in electrons, eg, with electrophilic reagents in electrophilic addition (6,7), free radicals in free-radical addition (8,9), and under acidic conditions with another butylene (cation) in dimerization.

Electrophile Addition. The addition of electrophilic (acidic) reagents HZ involves two steps: the slow transfer of hydrogen ion from :Z to the butylene to form a carbocation; and, a rapid combination of the carbocation with the base :Z.



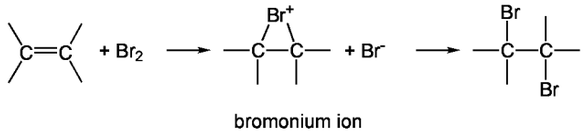
where HZ = HCl, HBr, HI, H_2SO_4, H_3O^+

The rate of addition depends on the concentration of both the butylene and the reagent HZ. The addition requires an acidic reagent and the orientation of the addition is regioselective (Markovnikov). The relative reactivities of the isomers are related to the relative stability of the intermediate carbocation and are isobutylene ≫ 1 butene > 2 butenes. Addition to the 1-butene is less hindered than to the 2-butenes. For hydrogen bromide addition, the preferred orientation of the addition can be altered from Markovnikov to anti-Markovnikov by the presence of peroxides involving a free-radical mechanism.

Sulfuric acid is about one thousand times more reactive with isobutylene than with the 1- and 2-butenes, and is thereby very useful in separating isobutylene as *tert*-butyl alcohol from the other butenes. The reaction is simply carried out by bubbling or stirring the butylenes into 45–60% H_2SO_4. This results in the formation of *tert*-butyl hydrogen sulfate. Dilution with water followed by heat hydrolyzes the sulfate to form *tert*-butyl alcohol and sulfuric acid. The Markovnikov addition implies that isobutyl alcohol is not formed. The hydration of butylenes is most important for isobutylene, either directly or via the butyl hydrogen sulfate.

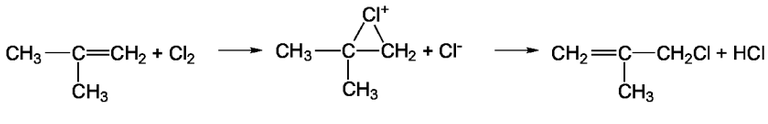
Certain oxidizing agents convert butylenes into 1,2-diols. Of the numerous oxidizing agents that bring about hydroxylation, two of the most commonly used are cold alkaline potassium permanganate, $KMnO_4$, and peroxy acids such as peroxyformic acid, HCO_2OH. Aqueous hydrolysis of the intermediate epoxide is required. $KMnO_4$ gives syn-addition whereas peroxyformic acid gives antiaddition.

Bromine and chlorine convert the 1- and 2-butenes to compounds containing two atoms of halogens attached to adjacent carbons (vicinal dihalides). Iodine fails to react. In this two-step addition mechanism the first step involves the formation of a cation. The halonium ion formed (a three-membered ring) requires antiaddition by the anion.



bromonium ion

Addition to *cis*- and *trans*-2-butene therefore yields different optical isomers (10,11). The failure of chlorine to attack isobutylene is attributed to the high degree of steric hindrance to approach by the anion. The reaction intermediate stabilizes itself by the loss of a proton, resulting in a very rapid reaction even at ambient temperature (12).



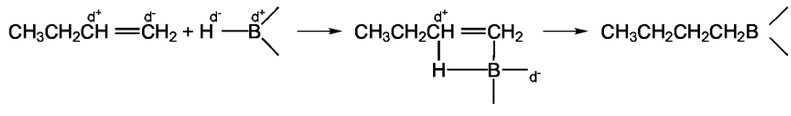
Addition of chlorine or bromine in the presence of water can yield compounds containing halide and hydroxyl on adjacent carbon atoms (haloalcohols or halohydrins). The same products can be obtained in the presence of methanol (13) or acetic acid (14). As expected from the halonium ion intermediate, the addition is anti. As expected from Markovnikov's rule, the positive halogen goes to the same carbon that the hydrogen of a protic reagent would.

Butylenes can be catalytically hydrogenated in the presence of Pt, Pd, or Ni in an exothermic reaction. In the absence of a catalyst, this reaction proceeds at a negligible rate, even at elevated temperatures. Heats of hydrogenation in kJ mol are as follows: 1-butene, 126.8; isobutylene, 118.8; *cis*-2-butene, 119.7; and *trans*-2-butene, −115.5.

Since a carbocation can add to an alkene to form a larger cation, under acidic conditions isobutylene can dimerize to form 2,4,4-trimethyl-1-pentene *[107-39-1]* and 2,4,4-trimethyl-2-pentene *[107-40-4]*, which can then be hydrogenated in the presence of nickel to form isooctane *[540-84-1]*. This reaction is no longer of commercial significance.

Alkylation of isobutylene and isobutane in the presence of an acidic catalyst yields isooctane. This reaction proceeds through the same mechanism as dimerization except that during the last step, a proton is transferred from a surrounding alkane instead of one being abstracted by a base. The cation thus formed bonds with the base. Alkylation of aromatics with butylenes is another addition reaction and follows the same general rules with regard to relative rates and product structure. Thus 1- and 2-butenes yield *sec*-butyl derivatives and isobutylene yields *tert*-butyl derivatives.

Two other reactions of interest are oxymercuration–demercuration and hydroboration–oxidation. Both reactions amount to hydration of the double bond to the alcohol. The former gives Markovnikov addition whereas the latter yields anti-Markovikov addition. In the first reaction the butylene reacts in aqueous mercuric acetate to add —OH and —$HgOOCCH_3$, to the double bond. Then the —$HgOOCCH_3$ is replaced by —H from sodium borohydride. This reaction is very fast and proceeds with 90% yield. A mercurinium ion (in analogy with a halonium ion) is invoked to explain the addition products. In hydroboration, hydrogen and boron from BHR_2 add to the double bond, then the boron is displaced by hydrogen peroxide in alkaline solution. The intermediate here is a four-centered transition state. As boron gains the pi electrons it becomes increasingly willing to release the hydrogen (see HYDROBORATION).



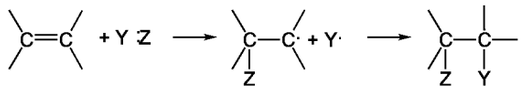
Butylene isomers also can be expected to show significant differences in reaction rates for metallation reactions such as hydroboration and hydroformylation (addition of $HCo(CO)_4$). For example, the rate of addition of di(*sec*-isoamyl)borane to *cis*-2-butene is about six times that for addition to *trans*-2-butene (15). For hydroformylation of typical 1-olefins, 2-olefins, and 2-methyl-1-olefins, specific rate constants are in the ratio 100:31:1, respectively.

The composition of the products of reactions involving intermediates formed by metallation depends on whether the measured composition results from kinetic control or from thermodynamic control. Thus the addition of diborane to 2-butene initially yields tri-*sec*-butylboraneTri-*sec*-butylborane. If heated and allowed to react further, this product isomerizes about 93% to the tributylborane, the product initially obtained from 1-butene (15). Similar effects are observed during hydroformylation reactions; however, interpretation is more complicated because the relative rates of isomerization and of carbonylation of the reaction intermediate depend on temperature and on hydrogen and carbon monoxide pressures (16).

These reactions are also quite sensitive to steric factors, as shown by the fact that if 1-butene reacts with di(*sec*-isoamyl)borane the initially formed product is 99% substituted in the 1-position (15) compared to 93% for unsubstituted borane. Similarly, the product obtained from hydroformylation of isobutylene is about 97% isoamyl alcohol and 3% neopentyl alcohol (17). Reaction of isobutylene with aluminum hydride yields only triisobutylaluminum.

Selectivity among butylene isomers also occurs in vapor-phase heterogeneous catalysis, at least in the case of dehydrogenation of butenes to butadiene, where maximum yields can be obtained by employing slightly different conditions for each isomer (18). In practice, mixtures of isomers are used and an average set of conditions is employed.

Free-Radical Addition. Free-radical attack on a butylene occurs so that the most stable radical carbon structure forms. Thus, in peroxide-catalyzed addition of hydrogen halides, the addition is anti-Markovnikov.



This reaction proceeds through a chain mechanism. Free-radical additions to 1-butene, as in the case of HBr, RSH, and H_2S to other olefins (19–21), can be expected to yield terminally substituted derivatives. Some polymerization reactions are also free-radical reactions.

Polymerization. Polymerization reactions, which are addition reactions, are used to produce the principal products formed directly from butylenes: butyl elastomers; polybutylenes; and polyisobutylene (see ELASTOMERS, SYNTHETIC; OLEFIN POLYMERS).

Substitution Reactions. The chemistry at alpha positions hinges on the fact that an allylic hydrogen is easy to abstract because of the resonance structures that can be established with the neighboring double bond. The allylic proton is easier to abstract than one on a tertiary carbon; these reactions are important in the formation of alkoxybutenes (ethers).

Isomerization. Isomerization of any of the butylene isomers to increase supply of another isomer is not practiced commercially. However, their isomerization has been studied extensively because: formation and isomerization accompany many refinery processes; maximization of 2-butene content maximizes octane number when isobutane is alkylated with butene streams using HF as catalyst; and isomerization of high concentrations of 1-butene to 2-butene in mixtures with isobutylene could simplify subsequent separations (22). One plant (Phillips) is now being operated for this latter purpose (23,24). The general topic of isomerization has been covered in detail (25–27). Isomer distribution at thermodynamic equilibrium in the range 300–1000 K is summarized in Table 4 (25).

Table 4. Equilibrium Butylenes Distribution, Ideal Gas[a,b]

	Mol %				
Temperature, K	1-Butene	*cis*-2-Butene	*trans*-2-Butene	Total butenes	Isobutylene
300	0.4	3.8	11.8	16.0	84.0
400	1.9	8.3	18.0	28.2	71.8
500	4.5	11.9	21.6	38.0	62.0
600	7.5	14.4	23.4	45.3	54.7
700	10.8	15.8	24.2	50.8	49.2
800	14.0	16.6	24.5	55.1	44.9
900	16.9	17.0	24.6	58.6	41.4
1000	19.6	17.2	24.4	61.2	38.8

[a] At 101.3 kPa 1 atm.

[b] Ref. 25.

The three isomerizations, *cis*-2-butene ⇌ *trans*-2-butene, 1-butene ⇌ 2-butene, and butenes ⇌ isobutylene, require increasingly severe reaction conditions. When the position of the double bond is shifted, cis–trans isomerization also occurs, and mixtures of butenes result when the carbon skeleton

is rearranged. However, during isomerization of 1-butene to 2-butene, with solid catalysts, the cis isomer is preferentially formed initially even though it is the thermodynamically less favored isomer.

An extremely wide variety of catalysts, Lewis acids, Brunsted acids, metal oxides, molecular sieves, dispersed sodium and potassium, and light, are effective (Table 5). Generally, acidic catalysts are required for skeletal isomerization and reaction is accompanied by polymerization, cracking, and hydrogen transfer, typical of carbenium ion intermediates. Double-bond shift is accomplished with high selectivity by the basic and metallic catalysts.

Table 5. Isomerization of Butylenes

Catalyst	Temperature, °C	References
	cis-2-Butene ⇌ *trans-2-butene*	
^{0}Co γ-rays	ambient	28
Na mordenite and porous Vycor	24.5	28
bis(acetylacetonato)Pd–SiO_2	61.5	29
	1-Butene ⇌ *2-butene*	
Pt–SiO_2–Al_2O_3	10	30
$RhCl_3$–$SnCl_2$–CH_3OH	ambient	31
$Cl_2[(C_4H_9)_3P]_2Ni$–$(C_2H_5)_2AlCl$–SiO_2	ambient	32
BF_3–Al_2O_3	ambient	33
H_3PO_4, 85%	73	34
Ga_2O_3	190–330	35
iodine	200–250	36
$ZnCrFeO_4$	465	37
	Butene ⇌ *isobutylene*	
Pt–Al_2O_3–SiO_2	475	38
SiO_2	520	39

Manufacture

The C_4 isomers are almost always produced commercially as by-products in a petroleum refinery petrochemical process as shown in Figure 2. Environmental regulations mandated by recent changes in the laws of the United States to reduce the aromatic content in gasoline will have an impact on butylene production in this country. As petroleum refiners search for alternative routes to replace the aromatics in the gasoline pool, oxygenated hydrocarbons will become increasingly attractive, not only for regaining the lost octane value in the gasoline but also for producing a clean burning fuel. Among this class of oxygenates, methyl-*tert*-butyl ether (MTBE) produced from isobutylene appears to be a leading contender (see ETHERS). Free-standing facilities at the gas well head to produce an isobutylene-rich B–B stream cannot be ruled out in the future.

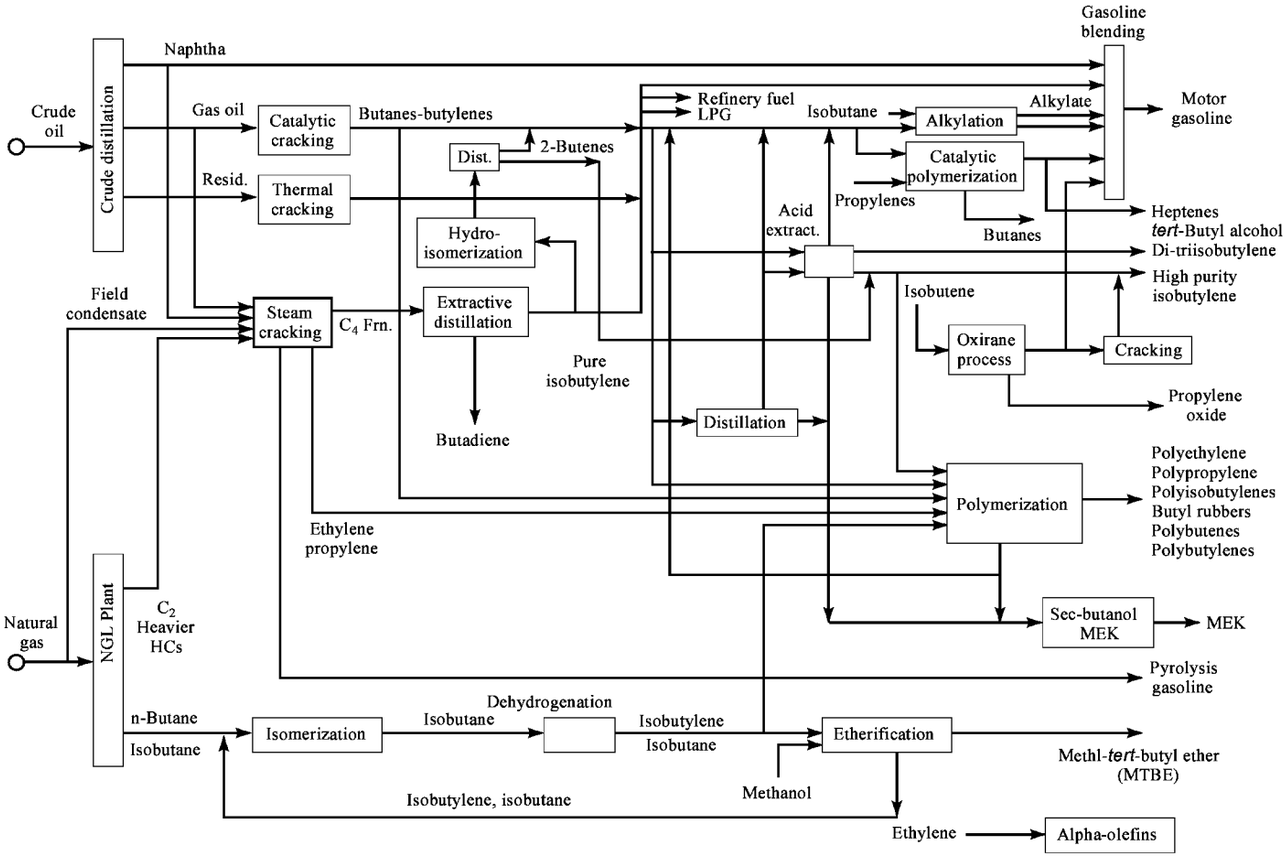


Fig. 2. General U.S. refinery-petrochemical system.

There are two important sources for the commercial production of butylenes: catalytic or thermal cracking, and steam cracking. In these two processes, butylenes are always produced as by-products. A catalytic cracking process is always associated with a petroleum refining complex that upgrades high boiling fractions of hydrocarbons to high octane gasoline. Steam cracking converts a variety of hydrocarbon feedstocks that range from natural gas liquids to heavy petroleum fractions to produce light olefins. As demand for butylenes picks up in the future, a third important source for the commercial

production of these products is likely to be the dehydrogenation of butanes.

There are other commercial processes available for the production of butylenes. However, these are site or manufacturer specific, eg, the Oxirane process for the production of propylene oxide; the disproportionation of higher olefins; and the oligomerization of ethylene. Any of these processes can become an important source in the future. More recently, the Coastal Isobutane process began commercialization to produce isobutylene from butanes for meeting the expected demand for methyl-*tert*-butyl ether (40).

Table 6 compares the total production of butylenes in the United States, Western Europe, and Japan. Included in this table are relative amounts of productions from different processes. In the United States, about 92% of the butylene production comes from refinery sources, whereas only about 45% in Western Europe and Japan are from this source. This difference arises because the latter cracks mostly petroleum distillates in the steam crackers that produce larger amounts of butylenes than the light feedstocks cracked in the United States.

Table 6. Butylene Availability in 1985, 10^3 t/yr[a]

Country	Refinery	Steam crackers	Total
United States	11,521	885	12,406
Western Europe	1,426	1,705	3,131
Japan	690	780	1,470
Total	*13,637*	*2,590*	*17,007*

[a] Courtesy of *Oil and Gas Journal* (Mar. 24, 1986).

Table 7 shows the yield distribution of the C_4 isomers from different feedstocks with specific processing schemes. The largest yield of butylenes comes from the refineries processing middle distillates and from olefins plants cracking naphtha. The refinery product contains 35 to 65% butanes; olefins plants, 3 to 5%. Catalyst type and operating severity determine the selectivity of the C_4 isomer distribution (41) in the refinery process stream. Processes that parallel fluid catalytic cracking to produce butylenes and propylene from heavy crude oil fractions are under development (42).

Table 7. Typical Yields and % Compositions of C_4 Fractions from Cracking Operations[a]

Butylene yield	Catalytic cracking			Thermal cracking of residue				Steam cracking of naphtha and light gas oil	
	Gas oil	Residue		Delayed coking		Flexicoking			
wt % on crude	0.5–5	1.5–3		0.1–0.6		0.15–0.8			
wt % on feed	3–10	3–5		1–1.5		1.5–2		0.4–0.5	
C_4 composition	Total	Olefin	Total	Total	Olefin	Total	Olefin	Total	Olefin
butane	7–13		7	47		14–23		2–5	
isobutane	28–52		18–14	12		5		1.5–0.6	
isobutylene	26–8	40–23	79	16	40	13	20–18	27.4–22.0	48
1-butene	8–7	12–20	79	13	31	17	26–24	16.0–14.0	30
cis-2-butene	31–20	48–57	75–79	5	12	35–42	54–58	5.5–4.8	10
trans-2-butene	31–20	48–57	70	7	17	35–42	54–58	6.5–5.8	12
1,3-butadiene	0.1–0.5			0.5		7–9		37.0–47.5	

[a] Ref. 43.

Steam Cracking. Steam cracking is a nonselective process that produces many products from a variety of feedstocks by free-radical reactions. An excellent treatise on the fundamentals of manufacturing ethylene has been given (44). Feedstocks range from ethane on the light end to heavy vacuum gas oil on the heavy end. All produce the same product slate but in different amounts depending on the feedstock.

Significant products from a typical steam cracker are ethylene, propylene, butadiene, and pyrolysis gasoline. Typical wt % yields for butylenes from a steam cracker for different feedstocks are ethane, 0.3; propane, 1.2; 50% ethane 50% propane mixture, 0.8; butane, 2.8; full-range naphtha, 7.3; light gas oil, 4.3. A typical steam cracking plant cracks a mixture of feedstocks that results in butylenes yields of about 1% to 4%. These yields can be increased by almost 50% if cracking severity is lowered to maximize propylene production instead of ethylene.

Cracking conditions and feed slate are usually selected to maximize production of light olefins. Selectivity to light olefins depends on the temperature and pressure profiles in the pyrolysis reactor coil, and thus the residence time. These profiles are unique for a given reactor coil, so a great deal of attention goes into the selection of the reactor. Older plants that have a residence time of about 1 s have since been modernized to under 0.4 s by replacing the reactor coil. Newer plants have reactor coil designs that give residence times of 0.1–0.2 s.

Typically, cracking is done at a weight ratio of steam to hydrocarbon that ranges from 0.2 to 1. The high end of this ratio is used for heavy feeds such as vacuum gas oil. Desired cracking severity is achieved at 780–875°C at the reactor coil outlet and at slightly above 130 kPa (19 psi) pressure. Hot furnace effluent from the reactors is quenched rapidly to stop undesirable secondary reactions. Effluent streams are cooled quickly in heat exchangers to slightly above their dew point, about 120–370°C depending on the feedstock.

Figure 3 shows a typical arrangement of a steam cracker in the United States. Furnace effluent from a steam cracker consists of three phases at ambient temperatures including aqueous liquid, hydrocarbon liquid, and hydrocarbon gas. Effluent from the heat exchangers are further cooled in oil and water wash towers. The oil wash essentially removes the heavy fuel oil fraction and also limits the end point of pyrolysis gasoline in the overhead of this tower. The water wash condenses the dilution steam and the pyrolysis gasoline. The overhead from the water wash tower contains mostly C_4 and lighter fractions. Several fractionation sequences to separate high purity products are available commercially. The choice of sequence depends on the feed slate and economics. Figure 3 shows a front-end demethanizer scheme, which is usually used in steam crackers producing significant amounts of butylenes. Whatever the fractionation scheme used, the C_4 fraction is removed as overhead from the debutanizer. References 45 and 46 give an overview of the ethylene manufacturing process.

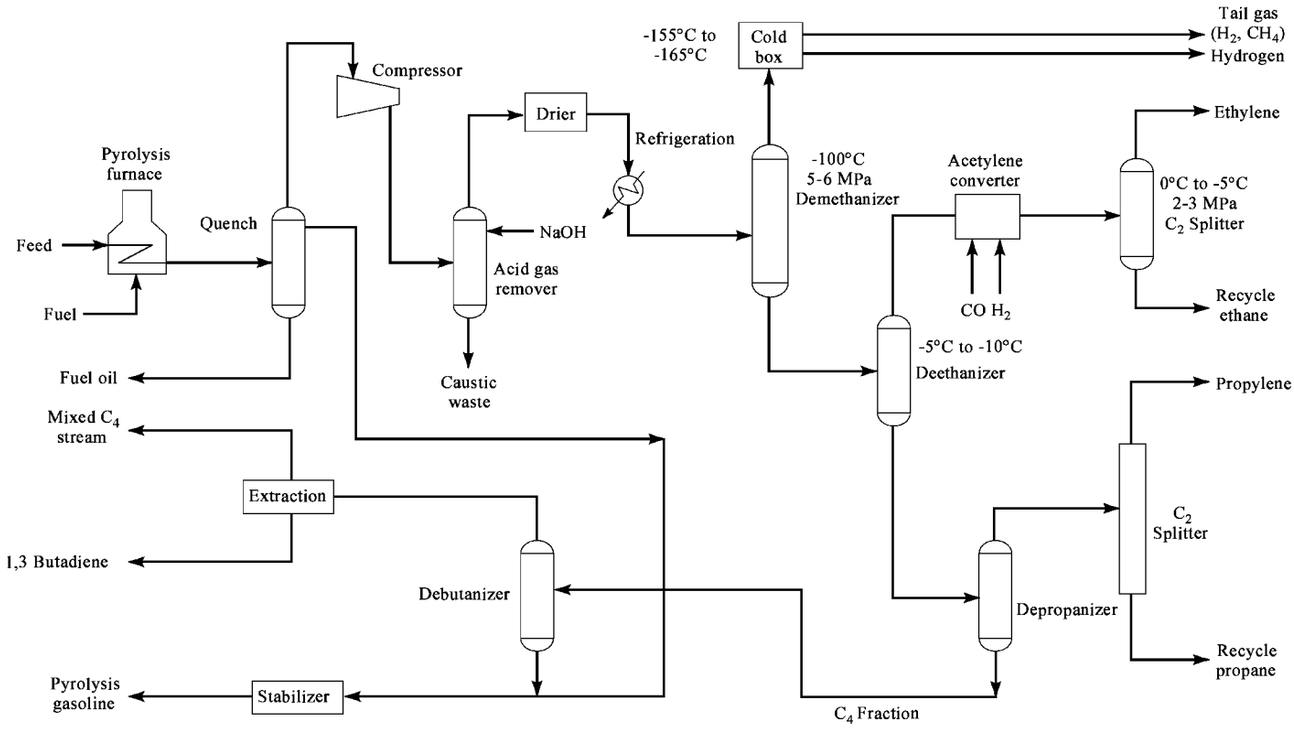


Fig. 3. Steam cracking front-end demethanizer scheme.

The C_4 stream from steam crackers, unlike its counterpart from a refinery, contains about 45% butadiene by weight. Steam crackers that process significant amounts of liquid feedstocks have satellite facilities to recover butadiene from the C_4 stream. Conventional distillation techniques are not feasible because the relative volatility of the chemicals in this stream is very close. Butadiene and butylenes are separated by extractive distillation using polar solvents.

The selection of solvent is dictated by the process used. Strongly dipolar, aprotic solvents alone or mixed with a second solvent to improve separation selectivity are used. The second solvent is usually water, and good solubility in water is an advantage. Toxicity is also an important consideration. Reference 47 is valuable in the selection of solvents. Several extractive distillation technologies are available commercially. Three technologies are used widely including the Nippon-Zein process using dimethylformamide *[68-12-2]* (48,49), the Shell process using acetonitrile *[75-05-8]* (50), and the BASF process using *N*-methyl-pyrrolidinone *[872-50-4]* (51). All these processes produce polymer-grade 1,3-butadiene and a B–B stream. C_4 Acetylenes and 1,2-butadiene in the B–B product are hydrogenated to produce a clean B–B stream.

Catalytic Cracking. This is a refinery process that produces a mixture of butylenes and butanes with very small amounts of butadiene. The specific composition of the C_4 mixture depends on the catalyst and process conditions. Most catalytic cracking processes employ temperatures about 450–650°C at pressures of about 250–400 kPa (36–58 psi). The two types of catalysts, the amorphous silica–alumina (52) and the crystalline aluminosilicates called molecular sieves or zeolites (53), exhibit strong carbonium ion activity. Although there are natural zeolites, over 100 synthetic zeolites have been synthesized and characterized (54). Many of these synthetic zeolites have replaced alumina with other metal oxides to vary catalyst acidity to effect different type catalytic reactions, for example, isomerization. Zeolite catalysts strongly promote carbonium ion cracking along with isomerization, disproportionation, cyclization, and proton transfer reactions. Because butylene yields depend on the catalyst and process conditions, Table 7 shows only approximations.

Zeolites have largely replaced the silica–alumina catalysts. In addition, the catalytic property is further improved by changing the silica and alumina ratio and by introducing cations such as hydrogen and sodium to impart specific catalytic properties. The most significant advance is in improved selectivity to gasoline range products and not in increased activity. Detailed information on the chemistry of catalytic cracking is available (55).

The most dominant catalytic process in the United States is the fluid catalytic cracking process. In this process, partially vaporized medium-cut petroleum fractions called gas oils are brought in contact with a hot, moving, freshly regenerated catalyst stream for a short period of time at process conditions noted above. Spent catalyst moves continuously into a regenerator where deposited coke on the catalyst is burnt off. The hot, freshly regenerated catalyst moves back to the reactor to contact the hot gas oil (see CATALYSTS, REGENERATION).

Thermal Cracking. Heavy petroleum fractions such as resid are thermally cracked in delayed cokers or flexicokers (44,56,57). The main products from the process are petroleum coke and off-gas which contain light olefins and butylenes. This stream also contains a considerable amount of butane. Process conditions for the flexicoker are more severe than for the delayed coker, about 550°C versus 450°C. Both are operated at low pressures, around 300–600 kPa (43–87 psi). Flexicokers produce much more linear butenes, particularly 2-butene, than delayed cokers and about half the amount of isobutylene (Table 7). This is attributed to high severity of operation for the flexicoker (43).

Oxirane Process. In Arco's Oxirane process, *tert*-butyl alcohol is a by-product in the production of propylene oxide from a propylene–isobutane mixture. Polymer-grade isobutylene can be obtained by dehydration of the alcohol. *tert*-Butyl alcohol *[75-65-0]* competes directly with methyl-*tert*-butyl ether as a gasoline additive, but its potential is limited by its partial miscibility with gasoline. Current surplus dehydration capacity can be utilized to produce isobutylene as more methyl-*tert*-butyl ether is diverted as high octane blending component.

Disproportionation of Olefins. Disproportionation or the metathesis reaction offers an opportunity to convert surplus olefins to other desirable olefins. Phillips Petroleum and Institut Français du Pétrole have pioneered this technology for the dimerization of light olefins. The original metathesis reaction of Phillips Petroleum was intended to convert propylene to 2-butene and ethylene (58). The reverse reaction that converts 2-butene in the presence of excess ethylene to propylene has also been demonstrated (59). A commercial unit with a capacity of about 136,000 t/yr of propylene from ethylene via 2-butene has been in operation in the Gulf Coast since 1985 (60,61). In this process, ethylene is first dimerized to 2-butene followed by metathesis to yield propylene. Since this is a two-stage process, 2-butene can be produced from the first stage, if needed. In the dimerization step, about 95% purity of 2-butene is achieved at 90% ethylene conversion.

In the Institut Français du Pétrole process (62), ethylene is dimerized into polymer-grade 1-butene (99.5% purity) suitable for the manufacture of linear low density polyethylene. It uses a homogeneous catalyst system that eliminates some of the drawbacks of heterogeneous catalysts. It also inhibits the isomerization of 1-butene to 2-butene, thus eliminating the need for superfractionation of the product (63,64). The process also uses low operating temperatures, 50–60°C, and pressures (65).

Many heterogeneous catalysts have been commercialized to dimerize ethylene to selectively yield 1-butene or 2-butene (66–70). Since ethylene is generally priced higher than butylenes, economics favor the production of butylenes from steam crackers, not from ethylene. An excellent review on

metathesis is available (71).

Oligomerization of Ethylene. 1-Butene is a small by-product in the production of linear alpha-olefins by oligomerization of ethylene. Linear alpha-olefins have one double bond at the terminal position and comprise the homologous series of compounds with carbon atoms between 4 and 19. The primary use of alpha-olefins is in the detergent industry. About 245,000 t yr of 1-butene was produced for chemical use in the Gulf Coast of the United States in 1988 (72).

New Technology. Several new technologies are emerging for the production of isobutylene to meet the expected demand for isobutylene: (*1*) deep catalytic cracking; (*2*) superflex catalytic cracking; (*3*) dehydrogenation of butanes; and (*4*) the Coastal process of thermal dehydrogenation of butanes. Of these, both the dehydrogenation technology and the high pressure thermal pyrolysis technology (the Coastal process) have been around for a long time. These technologies were not economical since inexpensive sources of butylenes were available from petroleum refineries and steam crackers. During the 1960s isobutane was in plentiful supply, and the first commercial unit using the Coastal process was built in 1969 at Corpus Christi, Texas, with a capacity of about 150 million t yr (40). The dehydrogenation technology was also in use where there was a surplus of inexpensive isobutane. Under the current climate where butylenes are expected to be in short supply, these two technologies are staging a comeback.

Deep Catalytic Cracking. This process is a variation of fluid catalytic cracking. It uses heavy petroleum fractions, such as heavy vacuum gas oil, to produce propylene- and butylene-rich gaseous products and an aromatic-rich liquid product. The liquid product contains predominantly benzene, toluene, and xylene (see BTX PROCESSING). This process is being developed by SINOPEC in China (42,73). SINOPEC is currently converting one of its fluid catalytic units into a demonstration unit with a capacity of 60,000 t yr of vacuum gas oil feedstock.

Superflex Catalytic Cracking. A new process called Superflex is being commercialized to produce predominantly propylene and butylenes from low valued hydrocarbon streams from an olefins complex (74). In this process, raffinates (from the aromatics recovery unit and the B–B stream after the recovery of isobutylene) and pyrolysis gasoline (after the removal of the C –C_8 aromatics fraction) are catalytically cracked to produce propylene, isobutylene, and a crude C –C_8 aromatics fraction. All other by-products are recycled to extinction.

Dehydrogenation of Butanes. These processes are based on the propane dehydrogenation technology commercialized about 35 years ago. Thermodynamics dictate that the operation be carried out at high temperatures and low pressures to improve selectivity. In the dehydrogenation process, conversion of feedstock is equilibrium limited, and thus conversions are low relative to steam cracking. Work has been carried out by Air Products, UOP, Shell, Ashland, ICI, Monsanto, Phillips, and Petrotex. Among these, five distinct technologies are available for converting isobutane to isobutylene. These technologies include Oleflex from UOP (75), Catofin from CDTECH (76), fluidized-bed from Snamprogetti (77), STAR from Phillips Petroleum (78), and Coastal Thermal Cracking from Foster-Wheeler (40,79).

The UOP Oleflex process uses a proprietary platinum catalyst. Dehydrogenation of isobutane to isobutylene is endothermic, and optimum catalyst activity is maintained by supplying the heat of reaction through interheaters. The catalyst system employs UOP's Continuous Catalyst Regeneration (CCR) technology. The bed of catalyst slowly flows concurrently with the reactants and is removed from the last reactor and regenerated in a separate section. The reconditioned catalyst is then returned to the top of the first reactor. The CCR process is usually applied in the reforming of naphtha to aromatics. When supply is limited, *n*-butane can be isomerized to isobutane using UOP's Butamer process (80). The Butamer process is a fixed-bed, vapor-phase catalytic process that uses organic halides as promoters.

The Catofin process, which was formerly the property of Air Products (Houdry Division), uses a proprietary chromium catalyst in a fixed-bed reactor operating under vacuum. There are actually multiple reactors operating in cyclic fashion. In sequence, these reactors process feed for about nine minutes and are then regenerated for nine minutes. The chromium catalyst is reduced from Cr^{6+} to Cr^{3+} during the regeneration cycle.

The Snamprogetti fluidized-bed process uses a chromium catalyst in equipment that is similar to a refinery catalytic cracker (1960s cat cracker technology). The dehydrogenation reaction takes place in one vessel with active catalyst; deactivated catalyst flows to a second vessel, which is used for regeneration. This process has been commercialized in Russia for over 25 years in the production of butenes, isobutylene, and isopentenes.

The Phillips Steam Active Reforming (STAR) process catalytically converts isobutane to isobutylene. The reaction is carried out with steam in tubes that are packed with catalyst and located in a furnace. The catalyst is a solid, particulate noble metal. The presence of steam diluent reduces the partial pressure of the hydrocarbons and hydrogen present, thus shifting the equilibrium conditions for this system toward greater conversions.

The Coastal process uses steam pyrolysis of isobutane to produce propylene and isobutylene (as well as other cracked products). It has been suggested that the reaction be carried out at high pressure, >1480 kPa (~15 atm), to facilitate product separation. This process was commercialized in the late 1960s at Coastal's Corpus Christi refinery.

These processes are all characterized by low isobutane conversion to achieve high isobutylene selectivity. The catalytic processes operate at conversions of 45–55% for isobutane. The Coastal process also operates at 45–55% isobutane conversion to minimize the production of light ends. This results in significant raw material recycle rates and imposing product separation sections.

Dehydrogenation of isobutane to isobutylene is highly endothermic and the reactions are conducted at high temperatures (535–650°C) so the fuel consumption is sizeable. For the catalytic processes, the product separation section requires a compressor to facilitate the separation of hydrogen, methane, and other light hydrocarbons from-the paraffinic raw material and the olefinic product. An excellent overview of butylenes is available (81).

Separation and Purification of C_4 Isomers. 1-Butene and isobutylene cannot be economically separated into pure components by conventional distillation because they are close boiling isomers (see Table 1 and Fig. 1). 2-Butene can be separated from the other two isomers by simple distillation. There are four types of separation methods available: (*1*) selective removal of isobutylene by polymerization and separation of 1-butene; (*2*) use of addition reactions with alcohol, acids, or water to selectively produce pure isobutylene and 1-butene; (*3*) selective extraction of isobutylene with a liquid solvent, usually an acid; and (*4*) physical separation of isobutylene from 1-butene by absorbents. The first two methods take advantage of the reactivity of isobutylene. For example, isobutylene reacts about 1000 times faster than 1-butene. Some 1-butene also reacts and gets separated with isobutylene, but recovery of high purity is possible. The choice of a particular method depends on the product slate requirements of the manufacturer. In any case, 2-butene is first separated from the other two isomers by simple distillation.

There are currently three important processes for the production of isobutylene: (*1*) the extraction process using an acid to separate isobutylene; (*2*) the dehydration of *tert*-butyl alcohol, formed in the Arco's Oxirane process; and (*3*) the cracking of MTBE. The expected demand for MTBE will preclude the third route for isobutylene production. Since MTBE is likely to replace *tert*-butyl alcohol as a gasoline additive, the second route could become an important source for isobutylene. Nevertheless, its availability will be limited by the demand for propylene oxide, since it is only a coproduct. An alternative process is emerging that consists of catalytically hydroisomerizing 1-butene to 2-butenes (82). In this process, trace quantities of butadienes are also hydrogenated to yield feedstocks rich in isobutylene which can then be easily separated from 2-butenes by simple distillation.

The acid extraction process uses strong mineral acids, such as sulfuric, hydrochloric, and phosphoric. These acids selectively remove isobutylene from mixed butylenes. The Exxon, BASF, and the Compagnie Fran3aise de Raffinage (CFR) processes have been commercialized. A more recent process is the Nippon Petrochemical extraction process that uses hydrochloric acid along with a heavy-metal catalyst. It is available for licensing though it has not been commercialized (83,84). Reportedly, the selectivity to isobutylene hydration is significantly higher than in the sulfuric acid process. However, because of corrosion problems of stainless steel, this process requires titanium and palladium alloys.

There is little recent information on the Exxon and BASF processes (85–87). The CRF, Exxon, and BASF processes use sulfuric acid as the extraction medium. The BASF process is the dominant process in Europe. It uses the dilutest acid of any commercial process. This permits selective reaction even in the presence of butadiene. The BASF process uses vapor–liquid extraction unlike the Exxon and CRF processes which are of the liquid–liquid type.

The desired extraction process is the exothermic proton-catalyzed hydrolysis of isobutylene to *tert*-butyl alcohol. This alcohol is further dehydrated to yield pure isobutylene. At low concentrations the hydrolysis reaction is favored:

$$(CH_3)_2C \quad CH_2 + H_2O \quad \xrightarrow{H^+} (CH_3)_3COH$$

At high concentrations, there is a tendency to form an organic hydrosulfate:

$$(CH_3)_2C=CH_2 + H_2SO_4 \rightarrow (CH_3)_3CHSO_4$$

The main differences between these processes are the acid concentration and the extraction temperature to effect selective removal of isobutylene. The acid concentration range is 45–65% . Figure 4 shows a simplified flow diagram of the CFR process.

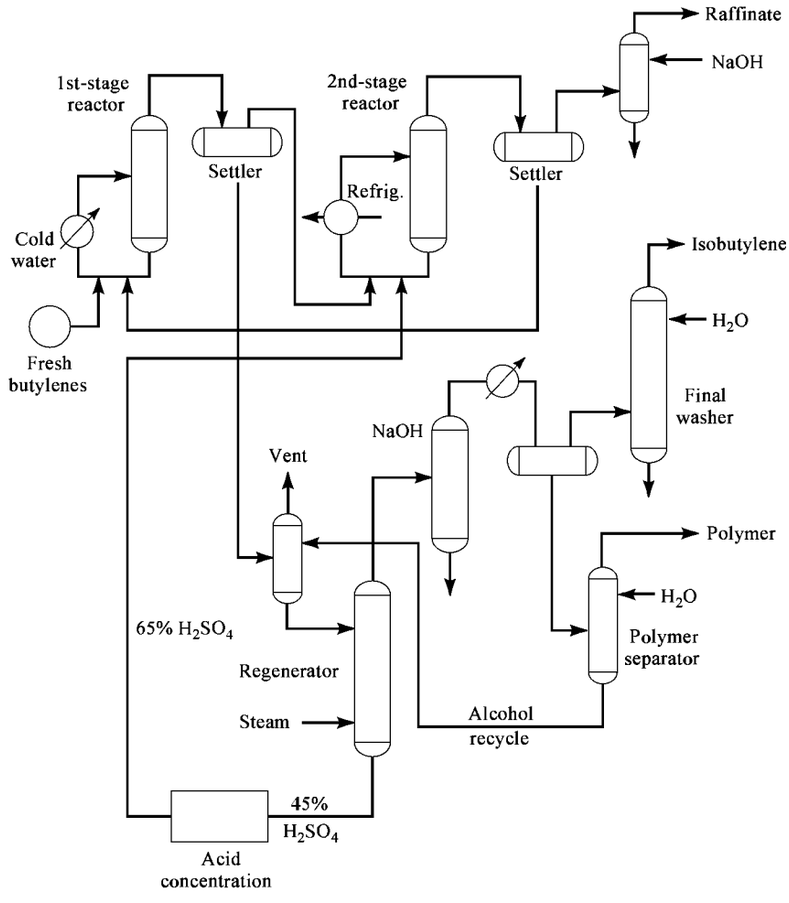


Fig. 4. Isobutylene extraction process.

In the physical separation process, a molecular sieve adsorbent is used as in the Union Carbide Olefins Siv process (88–90). Linear butenes are selectively adsorbed, and the isobutylene effluent is distilled to obtain a polymer-grade product. The adsorbent is a synthetic zeolite, Type 5A in the calcium cation exchanged form (91). UOP also offers an adsorption process, the Sorbutene process (92). The UOP process utilizes a liquid B–B stream, and uses a proprietary rotary valve containing multiple ports, which direct the flow of liquid to various sections of the adsorber (93,94). The cis- and trans-isomers are alkylated and used in the gasoline blending pool.

1-Butene can be separated from 2-butenes by simple distillation. If the B–B streams contain dienes, these must be hydrogenated prior to the separation of the linear butenes. If not hydrogenated, these contaminants tend to divide themselves between the purified isomers. Trace quantities of acetylinic compounds and butadiene are hydrogenated selectively using a noble metal catalyst. Hydrogenation after separation is not desirable as the catalyst used for hydrogenation isomerizes butenes, which affects product purity. If butanes are also present, as they are in the refinery streams, they also distribute themselves in the purified products. If pure isomers are required, butanes can be separated by extractive distillation, and the residual C_4 isomers can be isomerized. These all increase the cost of the separation process. There is a balance between the purity sought and the cost associated in achieving it.

Handling and Analysis

Storage and Transportation. Handling requirements are similar to liquefied petroleum gas (LPG). Storage conditions are much milder. Butylenes are stored as liquids at temperatures ranging from 0 to 40°C and at pressures from 100 to 400 kPa (1–4 atm). These conditions are much lower than those required for LPG. Their transportation is also similar to LPG; they are shipped in tank cars, transported in pipelines, or barged.

Analysis. Butenes are best characterized by their property of decolorizing both a solution of bromine in carbon tetrachloride and a cold, dilute, neutral permanganate solution (the Baeyer test). A solution of bromine in carbon tetrachloride is red; the dihalide, like the butenes, are colorless. Decoloration of the bromine solution is rapid. In the Baeyer test, a purple color is replaced by brown manganese oxide (a precipitate) and a colorless diol. These tests apply to all alkenes.

Identification of C_4 isomers is now routinely performed by gas chromatography. Advances in column technology permit rapid analysis with good accuracy in capillary columns (95). Pure isomers require quantification of contaminants, usually in parts per million. Gas–liquid chromatography and mass spectroscopy are the most commonly used analytical tools. The 1975 book of ASTM standards is an excellent reference listing several analytical procedures for hydrocarbon mixtures. Presently, Al_2O_3–KCl PLOT capillary gas chromatographic columns provide very good and fast separation in the following elution order: *trans*-2-butene, 1-butene, isobutylene, and *cis*-2-butene.

Health and Safety

Butylenes are not toxic. The effect of long-term exposure is not known, hence, they should be handled with care. Reference 96 lists air and water pollution factors and biological effects. They are volatile and asphyxiants. Care should be taken to avoid spills because they are extremely flammable. Physical handling requires adequate ventilation to prevent high concentrations of butylenes in the air. Explosive limits in air are 1.6 to 9.7% of butylenes. Their flash points range from 80 to 73°C. Their autoignition is around 324 to 465°C (Table 2). Water and carbon dioxide extinguishers can be used in case of fire.

Commercial Utilization

Pricing of butylenes determines the end use of butylenes in different geographic areas. The use pattern of butylenes in the United States, Europe, and Japan

is shown in Table 8 as a percentage of supply in 1984. Although the production of butylenes almost equals the production of ethylene or propylene, it has limited chemical use in these three geographic areas, averaging between 5 and 30% of total consumption. In the United States about 94% of butylenes are alkylated and used in the gasoline pool. The price for butylene in the United States is set at the alkylation value, which is always lower than its chemical value. In Europe and Japan, the refinery operation is set to produce more fuel oil, not just gasoline as in the United States. In these countries the main source of butylenes is from steam crackers. Because of lack of adequate LPG supply, these countries crack more naphtha to meet their demand for propylene. The coproduct butylenes are always in over supply in these countries, and their price is thus set at fuel value.

Table 8. Butylene Consumption, % of Supply[a]

Use	United States	Western Europe	Japan
	Fuel		
alkylate	85.6	22.1	2.0
methyl *tert*-butyl ether	4.5	8.2	0.0
polygas, LPG, blending	3.4	50.3	69.2
	Chemicals		
sec-butyl alcohol MEK	1.5	5.2	7.5
polyethylene copolymer	0.9	0.6	1.6
heptene, octene	0.7	3.4	1.3
butadiene	0.1	0.0	0.0
maleic anhydride	0.0	0.0	1.6
polybutene–polyisobutylenes	1.9	3.1	2.5
butyl rubbers	1.0	3.7	4.8
di- and triisobutylenes	~0.0	2.1	2.7
methyl methacrylate	0.0	0.0	4.4
other	0.4	1.3	2.4

[a] Ref. 97.

Among the butylenes, isobutylene has become one of the important starting materials for the manufacture of polymers and chemicals. There are many patents that describe the use of isobutylene or its derivatives to produce insecticides, antioxidants, elastomers, additives for lubricating oils, adhesives, sealants, and caulking compounds. Table 9 shows the use pattern of butylenes in the United States.

Table 9. Use Pattern for Butylenes in the United States in 1985[a]

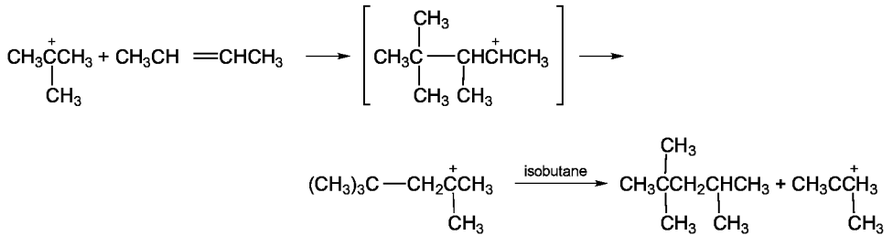
Product	Amount, 10^3 t	Isomer used
	Gasoline and fuels	
alkylate-polymer gasoline	11,524	mixed butylenes
direct blending and LPG	1,471	mixed butylenes
Total	*12,995*	
	Chemicals	
butadiene	78	butenes
sec-butyl alcohol	204	butenes
methyl *tert*-butyl ether	885	isobutylene
methyl methacrylate and methacrylic acid	0	mixed butylenes[b]
di- and triisobutylene	1.4	isobutylene
alkylated phenols, cresols	27	isobutylene
heptenes, octenes	83	mixed butylenes
tert-butylamine	4.5	isobutylene
tert-butyl alcohol	0	isobutylene
primary amyl alcohol	na	butenes
butylene oxide	2.7	butenes
methallyl chloride	2.7	isobutylene
p-tert-butyltoluene	0	isobutylene
neopentanoic (pivalic) acid	2.7	isobutylene
di- and triisobutyl aluminum	1.8	isobutylene
ethylene-butylene copolymer	98	butenes
butylated hydroxyanisole	1.8	isobutylene
Total	*1,393*	
	Polymers	
butyl elastomers	150	isobutylene
polybutenes	266	mixed butylenes
polyisobutylenes	23	isobutylene
poly(1-butene)	17	1-butene
Total	*456*	
Total consumption	*14,844*	

[a] Ref. 97

[b] Isobutylene content in mixed butylenes.

Fuels.

Alkylate. Alkylation means the chemical combination of isobutane with any one or a combination of propylene, butylenes, and amylenes to produce a mixture of highly branched paraffins that have high antiknock properties with good stability. These reactions are catalyzed by strong acids such as sulfuric or hydrofluoric acid and have been studied extensively (98–103). In the United States mostly butylenes and propylene are used as the olefins. The alkylate contains a mixture of isoparaffins, ranging from pentanes to decanes and higher, regardless of the olefins used. The dominant paraffin in the product is 2,2,4-trimethylpentane, also called isooctane. The reaction involves methide-ion transfer and carbenium-ion chain reaction, which is catalyzed by strong acid.



The C_7 and C_8 paraffins comprise about 90% of the alkylate; C_8 accounts for over 60%. Over 70% of the commercial alkylation processes employ sulfuric acid as the catalyst. Among the butylenes, 2-butene is superior to 1-butene. The C_3–C_4 fraction from the catalytic crackers is considered to be a superior feedstock to the alkylation unit.

Polymer Gasoline. Refinery trends tend to favor alkylation over polymerization. Unlike the alkylation process, polymerization does not require isobutane. The catalyst is usually phosphoric acid impregnated on kieselghur pellets. Polymerization of butylenes is not an attractive alternative to alkylation unless isobutane is unavailable. The motor octane number of polymer gasoline is also low, and there is considerable shrinkage in product volume. The only commercial unit to be built in recent years is at Sasol in South Africa. The commercial process was developed by UOP in the 1940s (104).

Gasoline Blending and LPG. Direct blending of butylenes into gasoline has the highest value since there is no shrinkage in product volume or conversion cost. The amount of butylenes that can be blended is limited by vapor-pressure specifications, amounting to only 8 to 10% of the gasoline pool. More butylenes could be used in winter to increase volatility for easy starting. In warm seasons, the butylenes have to be reduced to prevent vapor lock in the motor carburetor. Environmental concern in recent years has reduced the amount of butylenes, which could be blended into gasoline.

Since the heating values are similar to LPG, butylenes may be blended with LPG for bottle gas (105,106). In Europe, because LPG is unavailable, it is common to use butylenes as fuel. In the United States, butylenes have a higher value as an alkylate feed. LPG, which is readily available, is used as fuel instead.

Chemicals. Although the amount of butylenes produced in the United States is roughly equal to the amounts of ethylene and propylene produced, the amount consumed for chemical use is considerably less. Thus, as shown in Table 10, the utilization of either ethylene or propylene for each of at least five principal chemical derivatives is about the same or greater than the utilization of butenes for butadiene, their main use. This production is only about one-third of the total; the two-thirds is derived directly from butane. The underlying reasons are poorer price–performance compared to derivatives of ethylene and propylene and the lack of applications of butylene derivatives. Some of the C_4 products are more easily derived from 1-, 2-, and 3-carbon atom species, eg, butanol, 1,4-butanediol, and isobutyl alcohol (see ACETYLENE DERIVED CHEMICALS; BUTYL ALCOHOLS).

$$2\,CH_2{=}CH_2 \xrightarrow{[O]} 2\,CH_3CHO \longrightarrow CH_3CH{=}CHCHO \xrightarrow{H_2} CH_3CH_2CH_2CH_2OH$$

$$HC{\equiv}CH + 2\,CH_2O \xrightarrow{H_2} HOCH_2CH_2CH_2CH_2OH$$

$$CH_3CH{=}CH_2 \xrightarrow[H_2]{CO} CH_3CH_2CH_2CH_2OH + (CH_3)_2CHCH_2OH$$

Table 10. Utilization of Ethylene, Propylene, and Butylene for Production of Chemicals,[a] 10^3 t[b]

Ethylene[c]		Propylene[c]		Butylene[d]	
polyethylene, low density	4398	polypropylene	3283	butadiene	78
polyethylene, high density	3675	isopropyl alcohol	455	*sec*-butyl alcohol	204
vinyl chloride	1958	cumene	720	polybutenes	283
vinyl acetate	365	propylene oxide	858	polyisobutylenes	23
ethylene oxide	1537	acrylonitrile	942	dimers and trimers	1
				butyl rubbers	150
				methyl *tert*-butyl ether	576
				butylated phenols and cresols	27

[a] In 1989, unless otherwise indicated.
[b] Assumes 100% conversion of olefins to products.
[c] Ref. 107.
[d] Ref. 97, in 1985.

The value of butylenes in the United States is determined by their value in alkylation of isobutane to high octane gasoline. Table 11 shows how the chemical use of ethylene, propylene, butylenes, and butanes varied between 1983 and 1988 and their corresponding price swings.

Table 11. Prices and Chemical Use for Ethylene, Propylene, Butylenes, and Butanes in the United States between 1983 and 1988[a]

Compound	Chemical use, 10^3 t yr	Price, $ t
ethylene[b]	13,009–15,853	309–419
propylene[b]	6,332–8,627	308–397
butylenes	200–824	130–510 (butenes)
		375–617 (isobutylene)
n-butane	880–1,080	
isobutane	163–311	154–309

[a] Ref. 108.
[b] Through 1987.

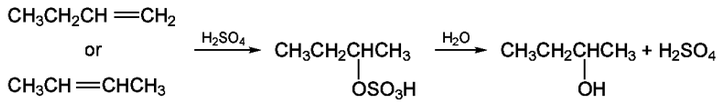
The price of butanes and butylenes fluctuates seasonally depending on the demand for gasoline in the United States. Since much chemical-product usage is determined by price–performance basis, a shift to development of butylene-based technology may occur. Among the butylenes, demand for isobutylene is likely to increase (and so its price) as more derivatives such as methyl methacrylate and methacrylic acid are produced from isobutylene instead of the conventional acetone cyanohydrin process.

Butadiene. Most butadiene *[106-99-0]* is produced by extraction of C_4 streams from olefins units. Only about one-third of butadiene was

produced from butenes in the United States as early as 1979. In Western Europe and Japan hardly any butenes are used to produce butadiene. Butadiene requirements in these countries are entirely met by the extraction units, since they crack only naphthas and heavier hydrocarbon feedstocks. The recent trend in the United States is to rely on the extraction units for its requirements (see BUTADIENE).

sec-Butyl Alcohol. *sec*-Butyl alcohol *[78-92-2]* is produced entirely from butenes using indirect hydration with sulfuric acid. Nearly all of the *sec*-butyl alcohol is converted to methyl ethyl ketone (MEK) *[78-93-3]* by catalytic dehydrogenation. MEK is an outstanding solvent for a wide variety of coating resins. *sec*-Butyl alcohol growth rate is closely tied in with the demand for MEK.

A typical feed to a commercial process is a refinery stream or a steam cracker B–B stream (a stream from which butadiene has been removed by extraction and isobutylene by chemical reaction). The B–B stream is a mixture of 1-butene, 2-butene, butane, and isobutane. This feed is extracted with 75–85% sulfuric acid at 35–50°C to yield butyl hydrogen sulfate. This ester is diluted with water and stripped with steam to yield the alcohol. Both 1-butene and 2-butene give *sec*-butyl alcohol. The sulfuric acid is generally concentrated and recycled (109) (see BUTYL ALCOHOLS).



Di- and Triisobutylenes. Diisobutylene *[18923-87-0]* and triisobutylenes are prepared by heating the sulfuric acid extract of isobutylene from a separation process to about 90°C. A 90% yield containing 80% dimers and 20% trimers results. Use centers on the dimer, C_8H_1 , a mixture of 2,4,4-trimethylpentene-1 and -2. Most of the dimer-trimer mixture is added to the gasoline pool as an octane improver. The balance is used for alkylation of phenols to yield octylphenol, which in turn is ethoxylated or condensed with formaldehyde. The water-soluble ethoxylated phenols are used as surface-active agents in textiles, paints, caulks, and sealants (see ALKYLPHENOLS).

$$C_8H_{16} + C_6H_5OH \longrightarrow (C_8H_{17})C_6H_4OH \xrightarrow{n\ C_2H_4O} (C_8H_{17})\ C_6H_4\ (OCH_2CH_2)_nOH$$

The octylphenol condensate is used as an additive to lubricating oils and surface-active agents. Other uses of dimer are amination to octylamine and octyldiphenylamine, used in rubber processing; hydroformylation to nonyl alcohol for phthalate production; and carboxylation via Koch synthesis to yield acids in formulating paint driers (see DRYING).

Butylated Phenols and Cresols. Butylated phenols and cresols, used primarily as oxidation inhibitors and chain terminators, are manufactured by direct alkylation of the phenol using a wide variety of conditions and acid catalysts, including sulfuric acid, *p*-toluenesulfonic acid, and sulfonic acid ion-exchange resins (110,111). By use of a small amount of catalyst and short residence times, the first-formed, ortho-alkylated products can be made to predominate. For the preparation of the 2,6-substituted products, aluminum phenoxides generated *in situ* from the phenol being alkylated are used as catalyst. Reaction conditions are controlled to minimize formation of the thermodynamically favored 4-substituted products (see ALKYLPHENOLS). The most commonly used is *p-tert*-butylphenol *[98-54-4]* for manufacture of phenolic resins. The *tert*-butyl group leaves only two rather than three active sites for condensation with formaldehyde and thus modifies the characteristics of the resin.

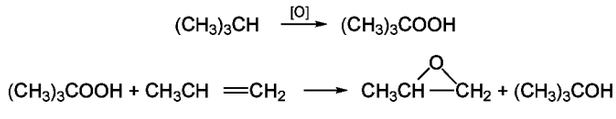
2,6-Di-*tert*-butyl-4-methylphenol *[25377-21-3]*2,6-Di-*tert*-butyl-4-methylphenol (di-*tert*-butyl-*p*-cresolDi-*tert*-butyl-*p*-cresol or butylated hydroxytoluene (BHT)) is most commonly used as an antioxidant in plastics and rubber. Use in food is decreasing because of legislation and it is being replaced by butylated hydroxy anisole (BHA) (see ANTIOXIDANTS; FOOD ADDITIVES).

Heptenes. Heptenes, C_7H_{14}, are used for the preparation of isooctyl alcohol *[26952-21-6]* by hydroformylation (see OXO PROCESS). The heptenes are prepared by very carefully controlled fractionation of polymer gasoline. Specifications generally call for >99.9% C_7 content (including some paraffin that is also formed) to simplify processing.

tert-Butylamine. *tert*-Butylamine *[75-64-9]* is used as an intermediate in the manufacture of lubricating oil additives and miscellaneous chemicals. It is manufactured using the Ritter reaction. Isobutylene first reacts with sulfuric acid and then HCN to yield *tert*-butylamine.

$$(CH_3)_2C{=}CH_2 \xrightarrow{H_2SO_4} (CH_3)_3COSO_3H \xrightarrow{HCN} (CH_3)_3CN{\rightarrow}CHOSO_3H \xrightarrow{H_2O}$$
$$(CH_3)_3CNHCHO \xrightarrow{OH} (CH_3)_3CNH_2$$

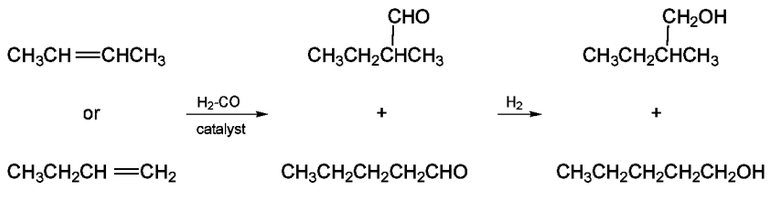
tert-Butyl Alcohol. *tert*-Butyl alcohol *[75-65-0]* is an intermediate in the separation of isobutylene from a mixed butane–butylene stream. It is manufactured by the hydrolysis of the acid extract in the isobutylene separation process. A small amount is used (about 5,000 t yr) as a solvent. It is also a significant coproduct (332,000 t yr) in Arco's Oxirane process (112) which produces propylene oxide *[75-56-9]* (253,000 t yr). *tert*-Butyl alcohol is derived from isobutane, which is the oxygen carrier for the process:



It competes directly with MTBE as an octane enhancer in the gasoline pool. Since MTBE is more desirable than *tert*-butyl alcohol because of its total miscibility with gasoline, *tert*-butyl alcohol will be an important source of isobutylene used in the manufacture of MTBE. High purity isobutylene, C_4H_8, can be obtained by dehydration of *tert*-butyl alcohol, $C_4H_{10}O$.

tert-Butyl Mercaptan. *tert*-Butyl mercaptan *[75-66-1]* is used primarily as an odorant at <30 ppm for natural gas so that leaks can be easily detected. It is manufactured by the reaction of isobutylene and hydrogen sulfide in the presence of acid catalysts (113).

Primary Amyl Alcohols. Primary amyl alcohols (qv) are manufactured by hydroformylation of mixed butenes, followed by dehydrogenation (114). Both 1-butene and 2-butene yield the same product though in slightly different ratios depending on the catalyst and conditions. Some catalyst and conditions produce the alcohols in a single step. By modifying the catalyst, typically a cobalt carbonyl, with phosphorus derivatives, such as tri(*n*-butyl)phosphine, the linear alcohol can be the principal product from 1-butene.



The main use of the amyl alcohols is as esters such as acetates for solvents.

Di- and Triisobutylaluminums. Triisobutylaluminum *[100-99-2]* is prepared by reaction of isobutylene with aluminum at 80°C and 20.3 MPa (200 atm) of hydrogen (115). It is used as a catalyst for ethylene oligomerization to prepare even numbered, linear 1-olefins. Use of stochiometric quantities of triisobutylaluminum followed by oxidation of the resulting mixture of long-chain aluminum alkyls yields even numbered, terminal primary alcohols in the plasticizer and detergent range (116). Oxychem uses this process in the United States to manufacture plasticizer ($C_{-}C_{10}$) and detergent (C_1 –C_{22}) range alcohols (see ALCOHOLS, HIGHER ALIPHATIC).

Triisobutylaluminum is converted to diisobutylaluminum chloride *[1779-25-5]* and diisobutylaluminum hydroxide *[1191-15-7]*, which are used as

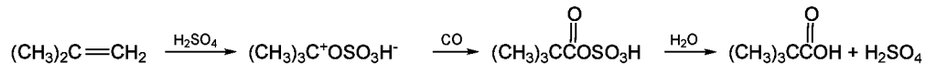
cocatalysts for Ziegler polymerization systems. Corresponding ethyl compounds are prepared via the reaction of triisobutylaluminum with ethylene.

Butylene Oxide. Butylene oxides are prepared on a small scale by Dow by chlorohydrin technology. There appears to be no technical reason why they could not be prepared by the propylene oxide Oxirane process (see CHLOROHYDRINS).

A significant use of butylene oxide *[26249-20-7]* is as an acid scavenger for chlorine-containing materials such as trichloroethylene. Inclusion of about 0.25–0.5% of butylene oxide, based on the solvent weight, during preparation of vinyl chloride and copolymer resin solutions minimizes container corrosion which may be detrimental to resin color and properties.

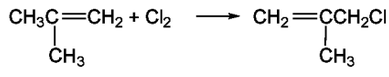
p-tert-Butyltoluene. *p-tert*-Butyltoluene *[98-51-1]*, prepared by acid catalyzed alkylation of toluene with isobutylene under mild conditions (117,118), is an intermediate in the production of *p-tert*-butylbenzoic acid *[98-73-7]*. This acid is used as a chain-length control agent in the preparation of unsaturated polyester resins. Solubility characteristics offer some advantage over benzoic acid.

Neopentanoic (Pivalic) Acid. Neopentanoic acid *[75-98-9]* is prepared using the Koch technology in which isobutylene reacts with carbon monoxide in the presence of strong acids such as H_2SO_4, HF, and $BF_3 \cdot H_2O$ (119–122). General reaction conditions are 2–10 MPa (about 20–100 atm) of CO and 40–150°C.



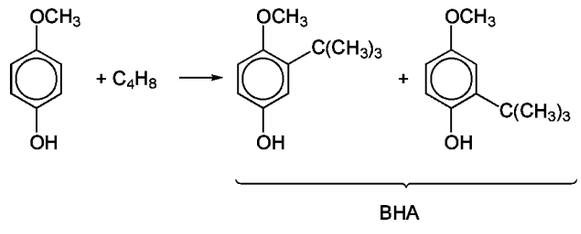
The acids are converted to peroxy esters for use as polymerization initiators. The metal salts are used as driers in paint formulations (see CARBOXYLIC ACIDS, TRIALKYLACETIC ACIDS).

Methylallyl Chloride. Methallyl chloride *[563-47-3]* is the principal product when isobutylene and chlorine react over a wide range of temperatures (123). Very little addition takes place.



This allylic chloride is a chemical intermediate for various specialty products, but it has no single significant commercial use (see CHLOROCARBONS AND CHLOROHYDROCARBONS, ALLYL CHLORIDE).

Butylated Hydroxy Anisole (BHA). This material is an oxidation inhibitor and has been accepted for use in foods where the use of butylated hydroxytoluene (BHT) is restricted (see FOOD ADDITIVES). It is manufactured by the alkylation of 4-hydroxyanisole *[150-76-5]* with isobutylene that yields a mixture of 2- and 3-*tert*-butyl isomers as products (124).



Methyl Methacrylate and Methacrylic Acid. The traditional production of methyl methacrylate *[80-62-6]* and methacrylic acid *[79-41-4]* involves the reaction of acetone with HCN and subsequent conversion to methyl ester and by-product ammonium bisulfate. Older plants in the United States with capacities in the range of 380,000 t yr still use this process.

The handling of toxic materials and disposal of ammonium bisulfate have led to the development of alternative methods to produce this acid and the methyl ester. There are two technologies for production from isobutylene now available: ammoxidation to methyl methacrylate (the Sohio process), which is then solvolyzed, similar to acetone cyanohydrin, to methyl methacrylate; and direct oxidation of isobutylene in two stages via methacrolein *[78-85-3]* to methacrylic acid, which is then esterified (125). Since direct oxidation avoids the need for HCN and NH_3, and thus toxic wastes, all new plants have elected to use this technology. Two plants, Oxirane and Rohm and Haas (126), came on-stream in the early 1980s. The Oxirane plant uses the coproduct *tert*-butyl alcohol directly rather than dehydrating it first to isobutylene (see METHACRYLIC ACID).

Methyl tert-Butyl Ether (MTBE). Methyl *tert*-butyl ether *[1634-04-4]* is made by the etherification of isobutylane with methanol, and there are six commercially proven technologies available. These technologies have been developed by Arco, IFP, CDTECH, Phillips, Snamprogetti, and Hüls (licensed jointly with UOP). The catalyst in all cases is an acidic ion-exchange resin. The United States has been showing considerable interest in this product. Western Europe has been manufacturing it since 1973 (ANIC in Italy and Hüls in Germany). Production of MTBE in Western Europe exceeded 600,000 tons in 1990.

The etherification reaction is equilibrium limited, requiring an excess of methanol to drive the reaction. Conversion is favored by low temperature whereas the reaction kinetics are favored by high temperature. A compromise on temperature must be made in order to obtain an economic design. The etherification reaction is exothermic, and these technologies differ primarily in the type of reactor employed and the method for removing heat of reaction. In these processes, the reaction is carried out in two reactors connected in series to facilitate heat removal and also for economic reactor design. Typically, isobutylene conversion is about 95%, with most of the conversion taking place in the first reactor. Units can also be designed to obtain greater than 99% conversion.

The first reactor in series in the Arco, IFP, and Phillips processes is adiabatic (vessel filled with catalyst). The exothermic heat of reaction is removed in a pump-around loop where a portion of the reactor contents are taken from the reactor, pumped through an external exchanger, cooled, and returned to the reactor.

The Snamprogetti process utilizes a tubular isothermal reactor (tubes filled with catalyst) for the first reactor with cooling water on the shell side to control temperature. The Hüls process uses either an adiabatic or isothermal reactor for the first reactor.

In the CDTECH process (formerly CR&L technology), the first reactor is adiabatic. The heat of reaction is removed partly by vaporization of the reaction mix. The operating temperature is controlled by adjusting the operating pressure.

The reactor combinations for the two reactors in series consist of two fixed-beds for the Arco process; an expanded bed followed by a catalytic distillation reactor for IFP; a fixed-bed followed by a catalytic distillation reactor for CDTECH; and two fixed-beds for Phillips. The Hüls process uses an adiabatic reactor for the second reactor.

The various sources of isobutylene are C_4 streams from fluid catalytic crackers, olefin steam crackers, isobutane dehydrogenation units, and isobutylene produced by Arco as a coproduct with propylene oxide. Isobutylene concentrations (weight basis) are 12 to 15% from fluid catalytic crackers, 45% from olefin steam crackers, 45 to 55% from isobutane dehydrogenation, and high purity isobutylene coproduced with propylene oxide. The etherification unit should be designed for the specific C_4 feedstock that will be processed.

Potential Use. Processes using butylenes as feedstocks have been developed for a group of industrial chemicals that are not currently produced by these processes or are produced only on a relatively small scale. Such chemicals are isoprene *[78-79-5]*, maleic anhydride *[108-31-6]*, acetic acid *[64-19-7]*, and until recently, methyl methacrylate and methyl *tert*-butyl ether. These processes are of interest because they may emerge as important processes with suitable improvements, changes in product values, or development of new markets.

Although current United States synthetic capacity for isoprene is based entirely on dehydrogenation of refinery isoamylenes and demethanation of

propylene dimer, there have been large amounts of work on alternative processes, particularly those using the Prins reaction (127–130). Processes have been developed both in Russia and by the Institute Fransais de Petrole. A significant advantage of the Prins reaction process is that isobutylene need not be first separated from the butane–butylene fraction because formaldehyde reacts selectively with the isobutylene.

A second route based on olefin disproportionation was developed by Phillips Petroleum (131). Here isobutylene reacts with propylene to form isoamylenes, which are dehydrogenated to isoprene. 2-Butene can be used in place of propylene since it also yields isoamylene and the coproduct propylene can be recycled. Use of mixed butylenes causes the formation of pentenes, giving piperylene, which contaminates isoprene.

Although the availability of butane–butylene streams containing high concentrations of isobutylene from steam crackers will increase and possibly make these technologies attractive, these same steam crackers also produce recoverable amounts of isoprene directly, particularly from heavier feedstocks.

Most maleic anhydride production in the United States is based on benzene as feedstock, even though substantial literature exists on the use of butenes (132–134). However, the rapidly increasing demand and price for benzene (as high as 620 $ t in 1986 versus 310 $ t for ethylene) have made benzene (qv) less attractive and butenes a better feedstock. Not only are theoretical yields better, 1.75 kg kg of butenes compared to 1.26 kg kg of benzene, but less oxygen is required and the oxidation produces less heat, which is critical in reactor design.

Although benzene prices have escalated in recent years, a concurrent need for butenes for use in alkylates for motor fuel has also increased and butane prices have also escalated. As a result, a search for alternative feedstocks began and Amoco Chemical Co. commercialized a process in 1977 to produce maleic anhydride from butane. A plant in Joliet came on-stream in 1977 with a capacity of 27,000 t yr (135,136). No new plants have been built in the United States based on butenes since the commercialization of butane to maleic anhydride technology. In Europe and particularly in Japan, however, where butane is in short supply and needs for butenes as alkylation feed are also much less, butenes may become the dominant feedstock (see MALEIC ANHYDRIDE).

A process to convert butenes to acetic acid has been developed by Farbenfabriken Bayer AG (137) and could be of particular interest to Europe and Japan where butylenes have only fuel value. In this process a butane–butylene stream from which butadiene and isobutylene have been removed reacts with acetic acid in the presence of acid ion-exchange resin at 100–120°C and 1500–2000 kPa (about 15–20 atm) (see ACETIC ACID AND ITS DERIVATIVES, ACETIC ACID). Both butenes react to yield *sec*-butyl acetate which is then oxidized at about 200°C and 6 MPa (about 60 atm) without catalyst to yield acetic acid.

This process may be competitive with butane oxidation (see HYDROCARBON OXIDATION) which produces a spectrum of products (138), but neither process is competitive with the process from synthesis gas practiced by Monsanto (139) and BASF (140) which have been used in 90% of the new acetic acid capacity added since 1975.

$$2\,H_2 + CO \longrightarrow CH_3OH \xrightarrow{CO} CH_3\overset{\overset{\displaystyle O}{\|}}{C}OH$$

Polymers account for about 3–4% of the total butylene consumption and about 30% of nonfuels use. Homopolymerization of butylene isomers is relatively unimportant commercially. Only stereoregular poly(1-butene) *[9003-29-6]* and a small volume of polyisobutylene *[25038-49-7]* are produced in this manner. High molecular weight polyisobutylenes have found limited use because they cannot be vulcanized. To overcome this deficiency a butyl rubber copolymer of isobutylene with isoprene has been developed. Low molecular weight viscous liquid polymers of isobutylene are not manufactured because of the high price of purified isobutylene. Copolymerization from relatively inexpensive refinery butane–butylene fractions containing all the butylene isomers yields a range of viscous polymers that satisfy most commercial needs (see OLEFIN POLYMERS; ELASTOMERS, SYNTHETIC BUTYL RUBBER).

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BUTYL RUBBER.

See ELASTOMERS, SYNTHETIC.

BUTYRALDEHYDES

The two isomeric butanals, *n*- and isobutyraldehyde, C_4H_8O, are produced commercially almost exclusively by the Oxo Reaction of propylene. They also occur naturally in trace amounts in tea leaves, certain oils, coffee aroma, and tobacco smoke.

Physical Properties

The butanals are highly flammable, colorless liquids of pungent odor. Their physical properties are shown in Table 1.

Table 1. Physical Properties of C-4 Aldehydes

	n-Butyraldehyde	Isobutyraldehyde
formula	$CH_3CH_2CH_2CHO$	$(CH_3)_2CHCHO$
CAS Registry Number	*[123-72-8]*	*[78-84-2]*
systematic name	butanal	2-methylpropanal
critical temperature, °C	263.95	233.85
critical pressure, kPa[a]	4000	4100
critical specific volume, m^3 (kg-mol)[b]	0.258	0.263
melting point, °C	96.4	65.0
normal boiling point, °C	74.8	64.1
coefficient of expansion at 20°C	0.00114	
refractive index at 25°C	1.3766	1.3698
liquid density at 20°C, kg m^3[c]	801.6	789.1
liquid heat capacity at 25°C, kJ (mol·K)[d]	0.16333	0.15581
heat of vaporization at normal boiling point, kJ mol[d]	30.72	31.23
ideal gas heat of formation at 25°C, kJ mol[d]	204.8	215.8
heat of fusion, kJ mol[d]	11.1	12.0
dipole moment, C·m[e]	9.07×10^{-30}	9.0×10^{-30}
dielectric constant ε at °C	13.426	
solubility parameter, at 25°C, $(MJ\ m^3)^{0.5}$[f]	18.666	18.446
solubility in water at 25°C, wt %	8.36	6.47
solubility of water in at 25°C, wt %	3.45	2.60

[a] To convert kPa to mm Hg, multiply by 7.50.
[b] To convert m^3 kg-mol to mL mol, multiply by 1000.
[c] To convert kg m^3 to g mL, divide by 1000.
[d] To convert kJ to kcal, divide by 4.184.
[e] To convert C·m to Debye, D, divide by 3.36×10^{-30}.
[f] To convert $(MJ\ m^3)^{0.5}$ to $(cal\ cc)^{0.5}$, multiply by $0.239^{0.5}$.

These aldehydes are miscible with most organic solvents, eg, acetone, ether, ethanol, and toluene, but are only slightly soluble in water. Some azeotropes of *n*-butyraldehyde are given in Table 2.

Table 2. Azeotropes of *n*-Butyraldehyde

Other component(s)	Wt %	Bp, °C
Homogeneous binary azeotropes		
ethanol	60.6	70.7
methanol	51	62.6
hexane (commercial)	74	60
Heterogeneous binary azeotropes		
water	12	68[a]
Heterogeneous ternary azeotropes		
ethanol	11	67.2[b]
water	9	

[a] The upper layer (94 vol %) contains 3.5 wt % water. The lower layer (6 vol %) contains 91.8% water.
[b] The upper layer (97.8 vol %) contains 11 wt % ethanol and 7 wt % water.

Reactions

The reactions of *n*- and isobutyraldehyde are characteristic aldehyde reactions of oxidation, reduction, and condensation.

Aldehydes (qv) are intermediate in the sequence:

$$\underset{\text{alcohol}}{RCH_2OH} \underset{\text{oxidation}}{\overset{\text{reduction}}{\rightleftharpoons}} \underset{\text{aldehyde}}{RCHO} \underset{\text{oxidation}}{\overset{\text{reduction}}{\rightleftharpoons}} \underset{\text{acid}}{RCOOH}$$

Thus, *n*-butyl [71-36-3] *[71-36-3]* and isobutyl alcohol [78-83-1] *[78-83-1]* are obtained by hydrogenation of their respective aldehydes and butyric and isobutyric acid are produced by oxidation.

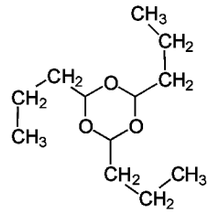
Hydrogenation of *n*- and isobutyraldehyde to the corresponding alcohols, $C_4H_{10}O$, can be carried out in high yield over various heterogeneous catalysts. Particularly effective in this application are $NiO–SiO_2–Al_2O_3$, Raney copper, and Raney nickel (1,2). Quantitative hydrogenation of butyraldehyde to butanol has also been effected with a homogeneous catalyst, $IrH_3[P(C_6H_5)_3]_2$, in acetic acid (3).

Oxidation of butyraldehyde to butyric acid *[107-92-6]* is most commonly carried out employing air or oxygen as the oxidant. Alternatively, organic oxidants, eg, cumene hydroperoxide, can also be employed effectively to give high yields of butyric acid, $C_4H_8O_2$ (4).

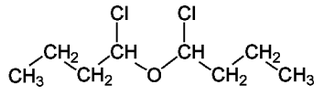
Catalytic oxidation of isobutyraldehyde with air at 30–50°C gives isobutyric acid *[79-31-2]* in 95% yield (5). Certain enzymes, such as horseradish peroxidase, catalyze the reaction of isobutyraldehyde with molecular oxygen to form triplet-state acetone and formic acid with simultaneous chemiluminescence (6).

Several species of bacteria under suitable conditions cause *n*-butyraldehyde to undergo the Cannizzaro reaction (simultaneous oxidation and reduction to butyric acid and butanol, respectively); this reaction can also be catalyzed by Raney nickel (7). The direct formation of butyl butyrate *[109-21-7]* or isobutyl isobutyrate *[97-85-8]* (Tishchenko reaction) from the corresponding aldehyde takes place rapidly with aluminum ethylate or aluminum butyrate as catalyst (8). An essentially quantitative yield of butyl butyrate, $C_8H_{16}O_2$, from butyraldehyde has been reported using a ruthenium catalyst, $RuH_2[P(C_6H_5)_3]_4$ (9).

Hydrogen chloride or a few drops of hydrochloric acid catalyze the conversion of *n*-butyraldehyde into the trimer, parabutyraldehyde, $C_{12}H_{24}O_3$, (2,4,6-tripropyl-1,3,5-trioxane *[56769-26-7]*, (1). The reaction is reversed by heating the parabutyraldehyde in the presence of acid. Anhydrous hydrogen chloride at 40°C converts *n*-butyraldehyde into 1,1′-dichlorodibutyl ether, (2) in 70–75% yield (10).



(1)



(2)

In the presence of dilute sodium or potassium hydroxide, *n*-butyraldehyde undergoes the aldol reaction to form 2-ethyl-3-hydroxyhexanal *[496-03-7]* which, on continued heating, is converted into 2-ethyl-2-hexenal *[26266-68-2]*. Hydrogenation of the latter gives 2-ethyl-1-hexanol *[104-76-7]*, a principal plasticizer alcohol.

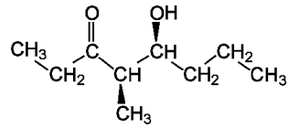
Many commercially important isobutyraldehyde derivatives are prepared through aldol and/or Tischenko condensation reactions. For example, isobutyraldehyde undergoes the aldol reaction to form isobutyraldol (2,2,4-trimethyl-3-hydroxypentanal *[918-79-6]*) which, when hydrogenated, gives 2,2,4-trimethyl-1,3-pentanediol (TMPD) *[144-19-4]*.

Isobutyraldehyde also undergoes consecutive aldol and Tischenko condensations to give 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate *[25265-77-4]* (Texanol, Filmer IBT), alternatively prepared by the esterification of TMPD with isobutyric acid.

Neopentyl glycol (2,2-dimethyl-1-propanol *[126-30-7]*), another important industrial derivative of isobutyraldehyde, is obtained from the aldol reaction product of isobutyraldehyde with formaldehyde followed by hydrogenation.

Crossed aldol reactions of butyraldehyde with other aldehydes also occur though these are generally not useful because they produce too many products. However, the commercially important solvent, methyl amyl ketone *[110-43-0]* is derived from the crossed aldol addition of acetone *[67-64-1]* with butyraldehyde. Similarly, formaldehyde *[50-00-00]* reacts cleanly with *n*-butyraldehyde to give 2,2′-(dihydroxymethyl)butanal *[41966-25-0]* (11), which can be hydrogenated to trimethylolpropane, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (TMP) *[77-99-6]*. Alternatively, formaldehyde and *n*-butyraldehyde react under hydrogen (6 MPa for 4 h at 70–120°C) over a $CuO–Al_2O_3$ catalyst in the presence of triethylamine, to give TMP in a single step in 85% yield (12). The reaction of formaldehyde with butyraldehyde, when carried out in the vapor phase (275–300°C) over a tungsten oxide on silica catalyst, gives 2-ethylacrolein *[922-63-4]* in 95% selectivity at 50% conversion (13).

n-Butyraldehyde undergoes stereoselective crossed aldol addition with diethyl ketone *[96-22-0]* in the presence of a stannous triflate catalyst (14) to give a predominantly erythro product (3). Other stereoselective crossed aldol reactions of *n*-butyraldehyde have been reported (15).



(3)

When the butanals are treated with alcohols in the presence of a mineral acid or calcium chloride, an acetal of the carbonyl group is produced.

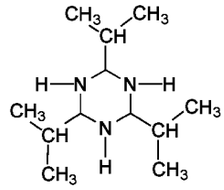
$$CH_3CH_2CH_2CHO + 2ROH \xrightarrow{H^+} CH_3CH_2CH_2CH(OR)_2 + H_2O$$

Reaction of poly(vinyl alcohol) *[9002-89-5]* with *n*-butyraldehyde yields poly(vinyl butyral) *[63148-65-2]* (PVB), a commercially important resin.

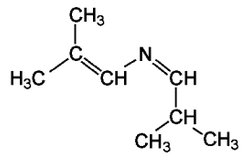
Various alkyl-substituted pyridine derivatives are formed from the condensation of butyraldehyde with ammonia at high temperatures. For example, cocondensation of *n*-butyraldehyde with acrolein *[107-02-8]* and ammonia at 400°C over a borosilicate zeolite gives 3-ethylpyridine *[536-78-7]* in 70% yield

(16). Similarly, condensation of *n*-butyraldehyde with ammonia over $Co_3Al_2(PO_4)_3$ at 350°C gives a 74% yield of 3,5-diethyl-2-propylpyridine *[4808-75-7]* (17).

Isobutyraldehyde reacts with aqueous ammonia at 0–10°C to give hexahydro-2,4,6-triisopropyl-*s*-triazine, (4) (18), whereas under refluxing conditions the eneazomethine *[5339-41-3]*, (5), is formed (19). Isobutyraldehyde condenses with two mole equivalents of urea in the presence of an acid catalyst to give isobutylidenediurea *[2224-20-6]* (IBDU), (6) a slow release fertilizer (20).



(4)



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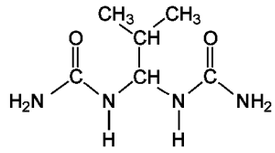
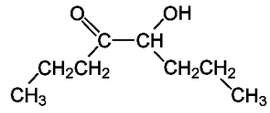


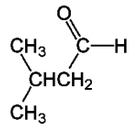
(6)

Butyraldehyde undergoes facile acyloin condensation via a novel thiazolium salt catalyzed procedure to give butyroin *[496-77-5]*, (7), in 71–74% yield (21).

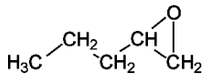
The butanals undergo some interesting homologation reactions employing certain quaternary triazolium or sulfonium salts as alkylating (homologating) agents. Isobutyraldehyde, for example, is converted into isovaleraldehyde *[590-86-3]*, (8), in 72% yield employing 3-methylthio-1,4-diphenyl-1,2,4-triazolium chloride (22). Similarly, *n*-butyraldehyde undergoes consecutive homologation and isomerization to 1,2-epoxypentane *[1003-14-1]*, (9), in 75% yield in the presence of dimethylhexylsulfonium methylsulfate (23).



(7)



(8)



(9)

Derivatives and Uses

The majority (92% in 1988) of the butyraldehyde produced in the United States is converted into 1-butanol and 2-ethylhexanol (2-EH). 2-EH is most widely used as the di(2-ethylhexyl) phthalate *[117-81-7]* ester for the plasticization of flexible PVC. Other uses for 2-EH include production of intermediates for acrylic surface coatings, diesel fuel, and lube oil additives (24).

The remaining (8%) *n*-butyraldehyde production of the United States goes into (in decreasing order): poly(vinyl butyral), 2-ethylhexanal, trimethylolpropane, methyl amyl ketone, and butyric acid.

Poly(vinyl butyral) is employed most widely as the adhesive interlayer in laminated automobile safety glass; it is also employed in architectural applications such as skylights, atriums, and glazing of office buildings. There are many grades of PVB. In general, 18–23% of the alcohol groups in the poly(vinyl alcohol) backbone remain unreacted, and there may be 1–3% residual ester groups from precursor poly(vinyl acetate).

2-Ethylhexanal, the reduced aldol condensation product of *n*-butyraldehyde, is converted into 2-ethylhexanoic acid *[149-57-5]*, which is converted primarily into salts or metal soaps. These are used as paint driers and heat stabilizers for poly(vinyl chloride).

Trimethylolpropane (TMP), the reduced crossed aldol condensation product of *n*-butyraldehyde and formaldehyde, competes in many of the same markets as glycerol (qv) and pentaerythritol. The largest market for TMP is as a precursor in unsaturated polyester resins, short-oil alkyds, and urethanes for surface coatings (see ALKYD RESINS).

Methyl amyl ketone, derived from the crossed aldol condensation of *n*-butyraldehyde and acetone, is used predominantly as a high solids coatings solvent. It is also employed as a replacement for the very toxic 2-ethoxyethyl acetate *[111-15-9]*.

Butyric acid, the simple oxidation product of *n*-butyraldehyde, is used chiefly in the production of cellulose acetate butyrate *[9004-36-8]*. Sheets of cellulose acetate butyrate are used for thermoformed sign faces, blister packaging, goggles, and face shields.

About 69% of the total 1988 U.S. consumption of isobutyraldehyde, went into the production of isobutyl alcohol and isobutyraldehyde condensation and esterification products. The other principal isobutyraldehyde derivative markets (as a percentage of total 1988 U.S. isobutyraldehyde consumption) are neopentyl glycol (15%); isobutyl acetate (6%); isobutyric acid (5%); isobutylidene diurea (2.5%); and methyl isoamyl ketone (1.7%).

2,2,4-Trimethyl-1,3-pentanediol (TMPD), the hydrogenated aldol condensation product of isobutyraldehyde, is a modifying agent in alkyd resins (qv), high solids coatings, and moisture-set inks.

The monoisobutyrate ester of TMPD, Texanol, or Filmer IBT, formally an isobutyraldehyde trimer, is prepared in a single step from isobutyraldehyde or, alternatively, by the esterification of TMPD with isobutyric acid. This monoester is most commonly employed as a coalescing agent for latex-based paints and water-based ink formulations.

The diisobutyrate ester *[6846-50-0]* of TMPD, Kodaflex TXIB, is used as a viscosity control agent in various plastisol, rotomolding, and rotocasting operations. Kodaflex TXIB is also used in the production of rolled sheet vinyl flooring where a high percentage of fugitive plasticizer flashes off during the fusion of the PVC resin to impart a harder flooring surface.

The principal markets for neopentyl glycol (NPG), the hydrogenated, crossed aldol condensation product of isobutyraldehyde and formaldehyde, are in water-borne and alkyd-surface coatings.

Isobutyl isobutyrate, the Tischenko condensation product of two molecules of isobutyraldehyde, is a slow evaporating ester solvent that has been promoted as a replacement for ethoxyethyl acetate. Although produced primarily by the acetylation of isobutyl alcohol, some isobutyl acetate is produced commercially by the crossed Tischenko condensation of isobutyraldehyde and acetaldehyde. Isobutyl acetate *[110-19-0]* is employed mainly as a solvent, particularly for nitrocellulose coatings.

Isobutyric acid, the simple oxidation product of isobutyraldehyde, is employed in the esterification of TMPD to form the mono- and diesters of TMPD. Some isobutyric acid is also used in the production of isobutyronitrile, an organo-phosphate pesticide precursor.

Isobutylidene diurea (IBDU), a slow release fertilizer, is formed from isobutyraldehyde and two moles of urea.

Methyl isoamyl ketone (MIAK), a product derived from the aldol condensation of isobutyraldehyde and acetone, is used principally as a solvent for lacquers, cellulosics, and epoxies.

Manufacture

The earliest commercial route to *n*-butyraldehyde was a multistep process starting with ethanol, which was consecutively dehydrogenated to acetaldehyde, condensed to crotonaldehyde, and reduced to butyraldehyde. In the late 1960s, production of *n*-butyraldehyde (and isobutyraldehyde) in Europe and the United States switched over largely to the Oxo reaction of propylene.

$$CH_3CH{=}CH_2 + CO + H_2 \xrightarrow{\text{Co or Rh}} CH_3CH_2CH_2CHO + (CH_3)_2CHCHO$$

The earliest modification of the Oxo process (qv) employed cobalt hydrocarbonyl, $HCo(CO)_4$, as catalyst. The reaction was carried out in the liquid phase at 130–160°C and 10–20 MPa (1450–2900 psi) to give a ratio of *n*- to isobutyraldehyde of between 2:1 to 4:1. *n*-Butyraldehyde, the straight-chain isomer and the precursor of 2-ethylhexanol, was the more valuable product so that a high isomer ratio of *n*- to isobutyraldehyde was obviously advantageous.

In the mid-1970s, a process employing a rhodium complex catalyst, $HRhCO[P(C_6H_5)_3]_3$, was commercialized by Union Carbide. This technology (25,26), subsequently licensed worldwide by Union Carbide and Davy McKee, operates at low temperatures 80–120°C and low pressure, 0.7–3 MPa (100–450 psi) and gives an isomer ratio of *n*- to isobutyraldehyde of 8:1 to 12:1. The advantages of the rhodium process for making butanals besides the lower temperatures and operating pressures, include a higher efficiency to the more valuable normal isomer and less by-product formation. The product butanals are separated continuously by vaporization from the nonvolatile catalyst, a distinct procedural advantage over the unmodified high pressure cobalt Oxo reaction. The latter requires a continuous separation and regeneration of the volatile cobalt hydrocarbonyl catalyst, which codistills with the butanal product. The rhodium catalyst, which is almost one thousand times more reactive than the cobalt hydrocarbonyl catalyst, requires relatively minute amounts of rhodium to achieve commercial rates of reaction.

In the mid-1980s, Ruhrchemie (now Hoechst) converted its oxo capacity to a proprietary water soluble rhodium catalyzed process (27,28), a technology developed jointly with Rhône-Poulenc. Product separation in this process is by decantation. Isomer ratios of *n*- to isobutyraldehyde of about 20:1 are obtained.

Mitsubishi Chemical uses a proprietary medium pressure rhodium-catalyzed process (29) in some plants which operate at 90–120°C and 5–10 MPa (725–1450 psi), and gives isomer ratios of about 4:1.

Quality Specifications

Some standard industrial quality specifications for *n*- and isobutyraldehyde are given in Table 3. Many times, however, specification limits are tailored to individual customer requirements.

Table 3. Quality Specifications for the Butanals

	n-Butyraldehyde[a]	Isobutyraldehyde[b]	Method[c]
aldehyde, wt %, min	98.5	99.5	capillary gc
distillation[d]	ibp 72.0°C min	ibp 62.5°C min	standard ASTM
	95 mL 80°C max	97 mL 67.0°C max	distillation for lacquer solvents
acidity	0.5 wt %, max[e]	0.2 wt %, max[e]	titration to phenolphthalein end point
water	0.3 wt %, max	0.07 wt %, max	Karl-Fischer titration
color	15 Pt–Co max	10 Pt–Co max	colorimetry
specific gravity at 20/20°C	0.801 to 0.806	0.788 to 0.793	densitometry
suspended matter	substantially free	substantially free	visual
iron	20 ppm max	20 ppm max	atomic absorption
copper		10 ppm max	atomic absorption
nickel		10 ppm max	atomic absorption
alcohols		0.3 wt %, max	capillary gc

[a] Ref. 30.

[b] Ref. 31.

[c] Refs. 32, 33.

[d] At 101.3 kPa (1 atm).

[e] Calculated as butyric acid.

Analysis

The butanals form the conventional aldehyde hydrazone, semicarbazone, and dimedone-type derivatives. In the absence of other aldehydes and ketones, *n*-butyraldehyde can be determined by addition of sodium bisulfite and the excess bisulfite determined with iodine or thiosulfate (34).

Analysis for the butanals is most conveniently carried out by gas chromatography. Trace quantities of *n*-butyraldehyde (18 ppb) in exhaust gases have been determined employing a combination of capillary gas chromatography with thermionic detection (35). Similarly, trace amounts of *n*-butyraldehyde in cigarette smoke and coffee aroma have been determined by various capillary gc techniques (36,37).

The infrared carbonyl stretching frequencies of *n*- and isobutyraldehyde in the condensed phase occur at 1727.6 and 1738.0 cm^{-1}, respectively (38). The proton nmr spectra of both aldehydes are well-known (39).

Economic Aspects

The total 1988 worldwide volumes of *n*- and isobutyraldehyde were $4.3-4.4 \times 10^6$ t and 7.7×10^5 t, respectively. The merchant market for the two aldehydes is relatively insignificant, most of the production being employed captively. The principal U.S. producers of butanals are given in Table 4. The principal producers in Western Europe and Asia are given in Table 5.

Table 4. U.S. Producers of Butanals[a]

Plant and location	Capacity, 10^3 t		Catalyst
	n-Butyraldehyde	Isobutyraldehyde	
Aristech Chemical Corp. Pasadena, Texas	114	11.4	Rh
BASF Corp. Freeport, Texas	99	19.5	Rh
Eastman Kodak Co. Longview, Texas	284	166	Co[b]
Hoechst Celanese Bay City, Texas	136	13.6	Rh
Union Carbide Corp. Texas City, Texas	330	33	Rh

[a] Ref. 24.

[b] Eastman converted to a new, low pressure catalyst in 1989.

Table 5. Western European and Asian Producers of Butanals[a]

Plant and location	Capacity, 10^3 t		Catalyst
	n-Butyraldehyde	Isobutyraldehyde	
Oxochimie Lavera, France	170	15	Rh
BASF AG Ludwigshafen, Germany	315	65	Rh
Hoechst AG Oberhausen, Germany	300	60	Co–Rh[b]
Huels AG Marl, Germany	300	25	Rh
BASF Espangnola, SA Tarragona, Spain	45	10	Rh
Neste Oxo AB Stenungsund, Sweden	180	15	Rh
Polimex Cekop Kedzierzen, Poland	135	14	Rh
Chisso Corp. Ichihara, Japan	65	7	Rh
Kyowa Yuka, Ltd. Yokkaichi, Japan	182	18	Rh
Mitsubishi Kasei Corp. Mizushima, Japan	210	40	Rh
Tonen Corp. Kawasaki, Japan	45	5	Rh
Lucky Chemical, Ltd. Naju, South Korea	124	11	Rh
China National Import Corp. Daqing, People's Republic of China	78	8	Rh
China National Import Corp. Qilu, People's Republic of China	78	8	Rh

[a] Ref. 24.

[b] About 86% of Hoechst's butanal is produced with the Rhône-Poulenc water-soluble rhodium catalyst; the remainder is still based on cobalt.

The overall growth for *n*-butyraldehyde depends primarily on *n*-butanol and 2-ethylhexanol. 2-Ethylhexanol is expected to face competition from other alcohols, eg, isodecyl alcohol *[25339-17-7]*, as well as from newer production sources.

n-Butanol is the highest volume derivative of *n*-butyraldehyde in the United States with nearly twice the production of 2-EH (56% vs. 36.5%). In sharp contrast, in Western Europe, Japan, and all other countries producing butyraldehydes, 2-EH is dominant.

The most active *n*-butyraldehyde derivatives are expected to be PVB, as more regions require automotive safety glass, and trimethylolpropane. Overall annual growth in *n*-butyraldehyde through 1993 is expected to be 0.9% in the United States and 1.2% in Japan. No growth in *n*-butyraldehyde consumption is expected in Western Europe through 1993.

Low pressure rhodium processes which give higher *n*:iso butyraldehyde ratios (eg, 10:1) have gradually replaced cobalt processes, dramatically effecting the isobutyraldehyde supply. Supply restraints and strong demand for certain value added derivatives will limit the overall growth of isobutyraldehyde to about 0.9% annually. The production of isobutyl alcohol the least valued isobutyraldehyde derivative, should actually decline as strong growth for neopentyl glycol and isobutyraldehyde condensation products limits the availability of isobutyraldehyde for conversion to isobutyl alcohol. As isobutyl and *n*-butyl alcohol prices approach parity some isobutyl alcohol consumers are expected to switch back to the normal isomer based on better solvency and perceived better performance.

Health, Safety, and Environmental Factors

Although tests have shown that *n*-butyraldehyde exhibits some adverse physiological effects, there is no danger to health in normal plant practice. No threshold limit value has been assigned for either butyraldehyde or isobutyraldehyde. Both aldehydes, however, have a pungent, penetrating odor. Their vapors as well as the neat liquids can cause skin, eye, and respiratory organ irritation possibly because of rapid oxidation to the acids on contact with air. Because of the ease of oxidation of the butanals to the corresponding butyric acids, precautions associated with these carboxylic acids must also be noted. Reported animal toxicity and irritancy values for the butanals are given in Table 6.

Table 6. Animal Toxicity and Irritancy Data for Butanals

	n-Butyraldehyde[a]	Isobutyraldehyde[b]
LD_{50}, oral, rats	5.9 mL kg	1.6–3.7 mL kg
LD_{50}, dermal, rabbits	1.26 mL kg	7.13 mL kg
inhalation, rats	4 h LC_{50} 16,400 (10,600 to 25,300) ppm	8,000 ppm killed 1 in 6 in 4 h
primary irritation, rabbits	grade 2 (no irritation on 3 rabbits, moderate capillary injection on 2)	grade 1 (no irritation)
eye injury, rabbits	grade 5 (severe corneal injury with iritis from 0.02 mL, moderate corneal injury from 0.005 mL)	grade 5 (severe corneal injury from 0.02 mL, minor from 0.005 mL)

[a] Ref. 40.
[b] Ref. 41.

The biological oxygen demand (BOD) in aqueous streams for both butanals is 1.62 wt wt for five days (42). The NFPA Hazard classification (42) for both aldehydes are health (blue) 2; flammability (red) 3; and reactivity (yellow) 0.

The flammability characteristics of the butanals are given in Table 7. The flash points for the butanals are well below room temperature. Thus, precautions must be taken to avoid heat, sparks, or open flame.

Table 7. Flammability Characteristics of Butanals

	n-Butyraldehyde	Isobutyraldehyde
flash point (closed cup), °C	11	40
autoignition temperature, °C	230	254
explosive limits in air, %	2.5–12.5	1.6–10.6

Both butanals are on the United States Toxic Substances Control Act (TSCA) Inventory, a prerequisite for the manufacture or importation for commercial sale of any chemical substance or mixture in quantities greater than one thousand pounds (455 kg). Additionally, the manufacture and distribution of the butanals in the United States are regulated under the Superfund Amendments and Reauthorization Act (SARA), Section 313, which requires that anyone handling at least ten thousand pounds (4550 kg) a year of a chemical substance report to both the EPA and the state any release of that substance to the environment.

Storage and Handling

Stainless steel, baked phenolic lined steel, or aluminum are often used for storage and handling of *n*- and isobutyraldehyde. The butanals are flammable and reactive, are easily oxidized on exposure to air, and in contact with acid, bases, or certain metal ions (eg, iron), will undergo exothermic condensation reactions. Storage of the aldehydes under nitrogen will avoid these problems and preserve the integrity of the material (43). There is some evidence that water stabilizes aldehydes against certain types of exothermic condensation reactions, possibly by precipitating any soluble iron species as hydrous iron oxides.

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BUTYRIC ACID AND BUTYRIC ANHYDRIDE.

See CARBOXYLIC ACIDS.

BUTYROLACTONE.

See ACETYLENE DERIVED CHEMICALS.

CABLE COVERINGS.

See INSULATION, ELECTRIC.

CACAO.

See CHOCOLATE AND COCOA.

CADMIUM AND CADMIUM ALLOYS

Cadmium *[7440-43-9]*, Cd, a Group 12 (IIB) element occurring between zinc and mercury, is a soft, ductile, silver-white metal having a distorted hexagonal close-packed structure (a = 0.29793 nm, c = 0.56181 nm). It was discovered in 1817 by Strohmeyer of Gottingen as an impurity in zinc carbonate. The crustal abundance of cadmium is somewhere between 0.1 and 0.5 ppm, and several cadmium minerals have been identified, the most common being greenockite *[1317-58-4]*, CdS. Cadmium is generally encountered in zinc ores, zinc-bearing lead ores, or complex copper–lead–zinc ores, however, where it forms an isomorphic impurity in the zinc mineral sphalerite *[12169-28-7]*, ZnS, usually in concentrations of 0.1–0.5% cadmium. For this reason, cadmium is almost invariably recovered as a by-product from the processing of zinc *[7440-66-6]*, lead *[7439-92-1]*, and copper *[7440-50-8]* ores.

Properties

Physical properties of cadmium are listed in Table 1. Its electronic structure is $1s^2 2s^2 2p\ 3s^2 3p\ 3d^{10} 4s^2 4p\ 4d^{10} 5s^2$, and its oxidation state in almost all of its compounds is +2, although a few compounds have been reported (1) in which cadmium exists in the +1 oxidation state. There are eight natural isotopes:

Mass	Relative abundance, %	Mass	Relative abundance, %
106	1.22	112	24.07
108	0.88	113	12.26
110	12.39	114	28.86
111	12.75	116	7.58

Table 1. Physical Properties of Cadmium

Property	Value
atomic weight	112.40
melting point, °C	321.1
boiling point, °C	767
latent heat of fusion, kJ/mol[a]	6.2
latent heat of vaporization, kJ/mol[a]	99.7
specific heat, J/(mol·K)[a]	
20°C	25.9
321–700°C	29.7
coefficient of linear expansion at 20°C, μm/(cm·°C)	0.313
electrical resistivity, μΩ·cm	
22°C	7.27
400°C	34.1
600°C	34.8
700°C	35.8
electrical conductivity, % IACS[b]	25
density, kg/m³	
26°C	8642
330°C (liq)	8020
400°C	7930

600°C	7720
volume change on fusion, % increase	4.74
thermal conductivity, W/(m·K)	
273 K	98
373 K	95
573 K	89
vapor pressure, kPa[c]	
382°C	0.1013
473°C	1.013
595°C	10.13
767°C	101.3
surface tension, mN/m(=dyn/cm)	
330°C	564
420°C	598
450°C	611
viscosity, mPa·s(=cP)	
340°C	2.37
400°C	2.16
500°C	1.84
600°C	1.54
molar magnetic susceptibility, cm^3/mol(=emu/mol)	-19.8×10^{-6}
Brinell hardness, kg/mm^2	16–23
tensile strength, MPa[d]	71
elongation, %	50
Poisson's ratio	0.33
modulus of elasticity, GPa[e]	49.9
shear modulus, GPa[e]	19.2
thermal neutron capture cross-section at 2200 m/s, m^2/atom	$2450 \pm 50 \times 10^{-28}$

[a] To convert J to cal, divide by 4.184.

[b] IACS = International Annealed Copper Standard.

[c] To convert kPa to mm Hg, multiply by 7.5.

[d] To convert MPa to psi, multiply by 145.

[e] To convert GPa to psi, multiply by 145,000.

Although it is only slowly oxidized in moist air at ambient temperature, cadmium forms a fume of brown-colored cadmium oxide *[1306-19-0]*, CdO, when heated in air. Other elements which react readily with cadmium metal upon heating include the halogens, phosphorus, selenium, sulfur, and tellurium.

The standard reduction potential for the reaction

$$Cd^{2+} + 2e \rightarrow Cd$$

is 0.402 V at 25°C (2). Cadmium is only slowly attacked by warm dilute hydrochloric or sulfuric acid resulting in the evolution of hydrogen. Because of its position in the electromotive series of elements, cadmium is displaced from solution by more electropositive metals such as zinc or aluminum.

Cadmium is rapidly oxidized by hot dilute nitric acid with the simultaneous generation of various oxides of nitrogen. Unlike the zinc ion, the cadmium ion is not markedly amphoteric, and therefore cadmium hydroxide *[21041-95-2]*, $Cd(OH)_2$, is virtually insoluble in alkaline media. However, the cadmium ion forms stable complexes with ammonia as well as with cyanide and halide ions. The metal is not attacked by aqueous solutions of alkali hydroxide.

Production

Cadmium occurs primarily as sulfide minerals in zinc, lead–zinc, and copper–lead–zinc ores. Beneficiation of these minerals, usually by flotation (qv) or heavy-media separation, yields concentrates which are then processed for the recovery of the contained metal values. Cadmium follows the zinc with which it is so closely associated (see ZINC AND ZINC ALLOYS; see also COPPER; LEAD).

The zinc concentrate is first roasted in a fluid-bed roaster to convert the zinc sulfide to the oxide and a small amount of sulfate. Normally, roasting is carried out with an excess of oxygen below 1000°C so that comparatively little cadmium is eliminated from the calcined material in this operation (3). Since the advent of the Imperial Smelting Zinc Furnace, the preliminary roasting processes for zinc and zinc–lead concentrates result in cadmium recovery as precipitates from solution or as cadmium–lead fume, respectively, as shown in Figure 1.

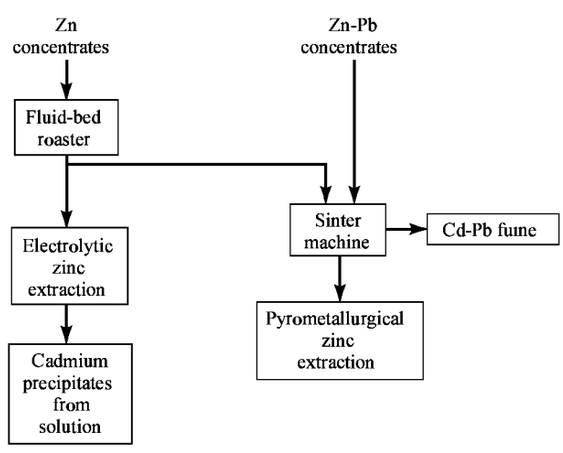

Fig. 1. Preliminary cadmium roasting processes.

Air pollution problems and labor costs have led to the closing of older pyrometallurgical plants, and to increased electrolytic production. On a worldwide basis, 77% of total zinc production in 1985 was by the electrolytic process (4). In electrolytic zinc plants, the calcined material is dissolved in aqueous sulfuric acid, usually spent electrolyte from the electrolytic cells. Residual solids are generally separated from the leach solution by decantation and the clarified solution is then treated with zinc dust to remove cadmium and other impurities.

Cadmium Precipitates. Processing (5) of the cadmium-bearing precipitate may follow the flow sheet shown in Figure 2. More recently, electrolytic zinc plant practice has developed such that precipitates containing up to 90% cadmium are produced and antimony is commonly used, instead of arsenic, as an additive in solution purification (7–11). The precipitates of Figure 2, containing 4 to 29 times more zinc than cadmium as well as other impurities, notably residual copper, is dissolved at 45–82°C in a mixture of spent electrolyte from the zinc plant, sulfuric acid, and spent cadmium electrolyte. The copper is removed by galvanic precipitation with a small amount of zinc dust. After filtering the copper cake, cadmium is reprecipitated in two stages, usually at pH 5.2 and using 0.6–2 kg zinc dust per kg cadmium, so that the product contains about 80% cadmium and less than 5% zinc. Steam oxidation of this sponge is optional. It is then dissolved at 45–82°C in spent cadmium electrolyte and make-up sulfuric acid to give a solution of about 200 grams Cd per liter, and is mixed with recirculating spent electrolyte to form the cell electrolyte. The electrowinning is carried out at 21–25°C in cells equipped with silver–lead anodes and aluminum cathodes at a current density varying between 26 and 240 A m^2, and cell voltages of 2.5–2.8 V. Glue is added at rates of 0–2.5 kilogram per metric ton of cadmium deposited. Cathode deposits are stripped from the aluminum blanks every 6 to 24 hours, depending on the current density. They are washed, dried, and melted at 380–400°C under sodium hydroxide, which not only acts as a flux to prevent oxidation, but also effectively removes any zinc or arsenic that may still be present. Finally, the metal is cast into commercial shapes, ie, slabs, balls, ingots, rods, splatters, and powder.

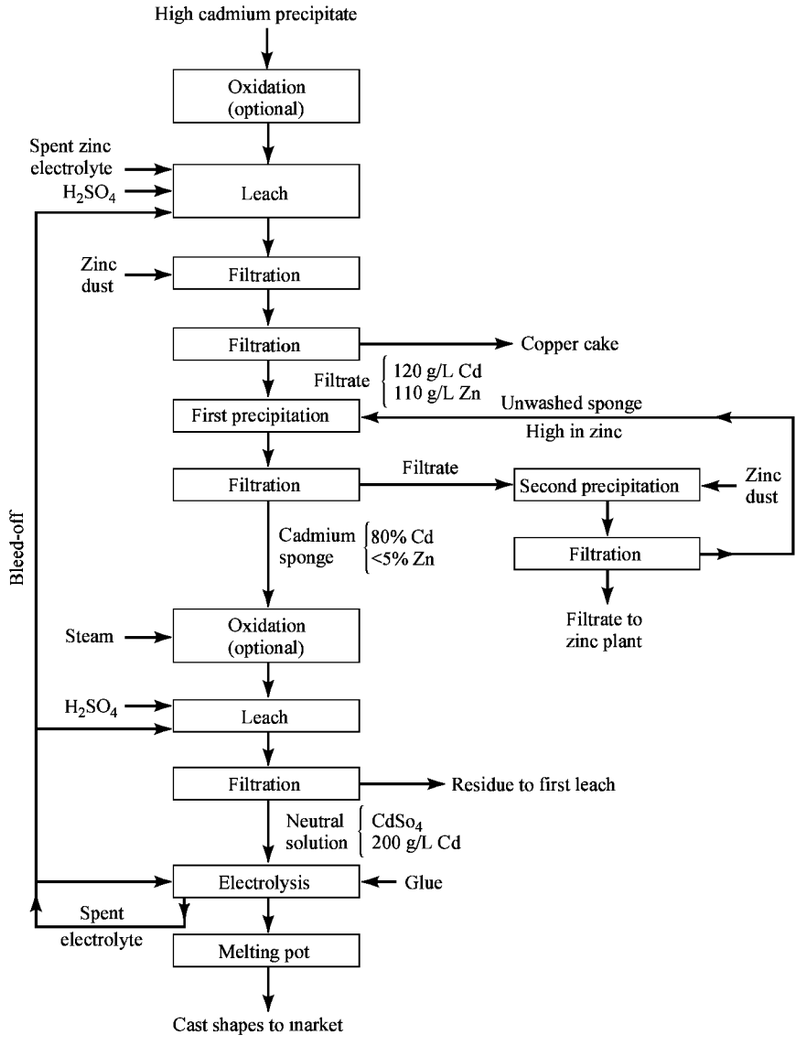

Fig. 2. Electrolytic production of cadmium from zinc electrolyte purification residue (5,6).

Precautions have to be taken during the dissolution of cadmium precipitates or the galvanic precipitation of cadmium with zinc to remove possible mist and toxic gases such as arsine. Suitable exhaust hoods and scrubbers must be provided. The fume that may be formed during cathode melting must be removed similarly.

Cadmium Fumes.

During the pyrometallurgical extraction of zinc, calcine from a roaster can be sintered with coke on a sintering machine to give a dense desulfurized product. The sintering operation results in considerable volatilization of cadmium and lead compounds, enhanced by the presence of chloride, leading to a 90–99% recovery of cadmium. The fume and dust from the sintering machine are collected in a baghouse (12,13). Cadmium not removed during sintering and subsequent operations follows the zinc metal and often is recovered during zinc metal purification by distillation.

The cadmium content in the feed to lead and copper smelters is lower than that generally encountered in zinc plants, and this necessitates upgrading the initial cadmium level in the fume by one or more refuming steps in a kiln or reverberatory furnace. The final fume may contain as much as 45% cadmium. In general, the composition of these fumes as well as those obtained from zinc sintering vary with respect to cadmium content and impurities. Fumes usually require more processing and purification steps for cadmium recovery than do purification residues from electrolytic zinc plants. Galvanic precipitation is the most frequently adopted method for the final recovery of cadmium in pyrometallurgical plants, but electrowinning may also be used (see METALLURGY, EXTRACTIVE).

The flow sheet in Figure 3 illustrates cadmium recovery from cadmium-bearing fumes. Depending on composition, the fume may have to be roasted with or without sulfuric acid or oxidized using sodium chlorate or chlorine in order to convert cadmium into a water- or acid-soluble form and to

eliminate volatile constituents. However the leach solution is obtained, it must generally be purified to remove arsenic, iron, copper, thallium, and lead, using the various treatments shown in Figure 3 for the recovery of cadmium from baghouse fume. The cadmium may also be galvanically precipitated from the leach solution and then redissolved (see *Alternative 1* in Fig. 3).

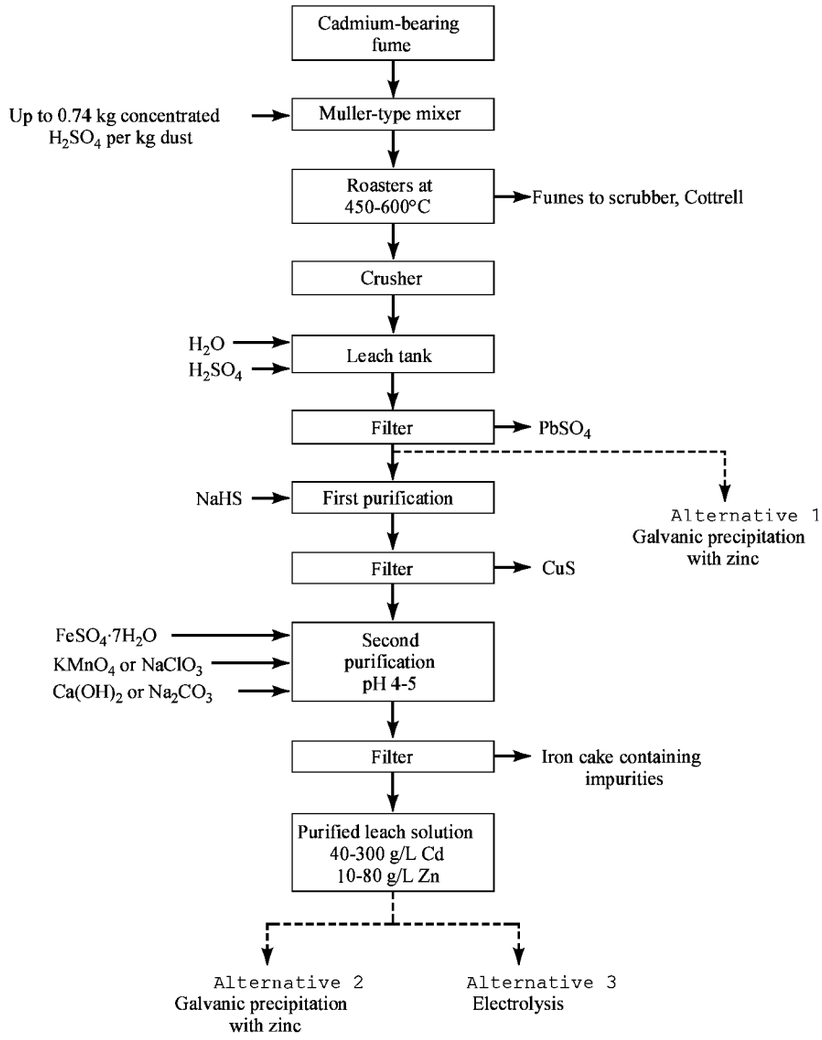

Fig. 3. Cadmium recovery from cadmium-bearing fumes (5).

In the recovery of cadmium from fumes evolved in the Imperial Smelting process for the treatment of lead–zinc concentrates, cadmium is separated from arsenic using a cation-exchange resin such as Zeocarb 225 or Amberlite 120 (14,15). Cadmium is absorbed on the resin and eluted with a brine solution. The cadmium may then be recovered directly by galvanic precipitation.

Alternative 2 in Figure 3 indicates the most common method for the recovery of cadmium from purified leach solution by galvanic displacement with zinc in the form of dust, sheets, or even rods or rectangular anodes. The final processing depends on the grade of zinc. In most cases, the pH for galvanic precipitation is below 2, although one plant operates at pH 6.2. Temperatures range from ambient to 70°C and precipitation times vary from 30 min to 18 h, depending on temperature and aggregation of the zinc. The weight of zinc required to precipitate one kilogram of cadmium varies between 0.65–0.95 kg. In most plants, the final cadmium sponge is washed to remove soluble impurities, and then compacted by briquetting. The briquettes may be melted under a flux of sodium hydroxide or ammonium chloride or be distilled for final purification.

In *Alternative 3* (Fig. 3), the electrolysis may be operated on a semicontinuous basis with the cadmium eventually being stripped completely from the electrolyte, which is then discarded after suitable treatment. Instead of the usual silver–lead anodes, high silicon–iron anodes, such as Duriron, are commonly used.

Economic Aspects

Cadmium production is dependent on the processing of zinc ores, which often contain 0.2 to 0.4% cadmium. As can be seen from Table 2, U.S. demand for cadmium normally exceeds the domestic supply and the United States is dependent on imports.

Table 2. United States Cadmium Statistics[a]

Year	Quantity, t			Average price, $ kg
	Production	Imports	Apparent consumption	
1984	1686	1889	3300	2.91
1985	1603	1988	3720	2.03
1986	1486	3174	4385	2.36
1987	1515	2701	4178	3.53
1988	1885	2482	3620	15.23
1989	1550	2787	4096	13.82
1990	1678	1741	3107	7.44
1991[b]	1600	2300	3500	4.51

[a] Ref. 16.
[b] Estimated. Courtesy of U.S. Bureau of Mines.

In 1988, cadmium metal production in the United States increased significantly and imports decreased, but exports increased. Dramatic increases in cadmium prices in 1988 were attributed to the tight supply of cadmium worldwide, heavy speculative trading, and the large quantities of cadmium being purchased by the nickel–cadmium battery industry, particularly in Japan. About 30 countries are cadmium producers, led by Russia, Japan, the United States, Canada, Belgium, Germany, and Mexico, which cumulatively represented 64% of the 1988 reported world cadmium production of 19,773 metric tons.

The apparent United States consumption of cadmium in 1988 was estimated to be 3620 t. Of the 2482 t imported, over 85% came from Canada, Mexico, Germany, and Australia. The principal domestic producers and suppliers of cadmium metal are ASARCO, Inc.; Big River Zinc Corp.; Jersey Minitre Zinc Co.; and Zinc Corp. of America.

The ASTM Standard Specification for Cadmium (B440) is for a minimum purity of 99.95%. Cadmium is also supplied in shot, 1–3 mm, to a purity of 99.9999%, priced at $361 kg in 1990.

Analysis

Although the most sensitive line for cadmium in the arc or spark spectrum is at 228.8 nm, the line at 326.1 nm is more convenient to use for spectroscopic detection. The limit of detection at this wavelength amounts to 0.001% cadmium with ordinary techniques and 0.00001% using specialized methods. Determination in concentrations up to 10% is accomplished by solubilization of the sample followed by atomic absorption measurement. The range can be extended to still higher cadmium levels provided that a relative error of 0.5% is acceptable. Another quantitative analysis method is by titration at pH 10 with a standard solution of ethylenediaminetetraacetic acid (EDTA) and Eriochrome Black T indicator. Zinc interferes and therefore must first be removed.

Safety and Handling

Cadmium is classified as a toxic metal. Acute industrial poisoning by cadmium dust or fume can occur during the melting or pouring of cadmium metal; the welding, burning, or heating of cadmium-plated steel; or spraying, brazing, and overheating of cadmium metal. Chronic poisoning has been reported in workers employed in casting cadmium alloys and in the manufacture of alkaline storage batteries (17). Protection should be provided by a properly designed exhaust ventilation system or, for some intermittent exposures, by a suitable individual filter or air-supplied respirator (18). Industrial exposure to cadmium fumes and dust has been reported to result in emphysema, hypertension, kidney failure, osteomalacia, and perhaps an increased incidence of cancer. Significant effects on worker health is rarely reported (19). Nevertheless, workers exposed to cadmium fumes or dust should be included in a medical surveillance program for pulmonary changes and renal function (20).

The 1991 Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL), 8-h time-weighted average standard (TWA) is 100 μg m^3 of air for cadmium fume, having a ceiling concentration of 300 μg m^3, and 200 μg m^3 of air for cadmium dust, 600 μg m^3 ceiling concentration. In 1990, the American Conference of Governmental Industrial Hygienists (ACGIH) specified a threshold limit value (TLV) and ceiling concentration of 50 μg m^3 for both cadmium fume and dust. However, in 1991 the ACGIH proposed a TLV of 10 μg m^3 total cadmium and 2 μg m^3 respirable fraction, along with an A2 suspected human carcinogen designation. Meanwhile, the National Institute of Occupational Safety and Health (NIOSH) recommended a PEL of 40 μg m^3 for both cadmium fume and dust at a 200 μg m^3 ceiling concentration for both. Finally, in 1991 OSHA proposed to lower the PEL to a level of 1 μg m^3 or 5 μg m^3 for cadmium and all cadmium compounds.

To help maintain the balance between supply and demand for cadmium, efforts can be made to recycle such cadmium-containing materials as spent nickel–cadmium batteries as well as dusts and other residues from the pigment industry. There are two principal ways to recover cadmium, either by hydrometallurgical or pyrometallurgical processes. Several hydrometallurgical methods have been proposed, such as recovery of cadmium and nickel sulfate from battery process wastes, but generally these methods are too complex and costly for large-scale applications. Pyrometallurgical methods employ either an open atmosphere where cadmium oxide is produced, or a reducing atmosphere where pure metallic cadmium results from distillation (21). Cadmium wastes that cannot be recycled should be discarded in accordance with local regulations governing disposal of hazardous wastes.

Uses

In 1988 the estimated apparent consumption pattern for cadmium was batteries (qv), 32%; coating and plating, 29%; pigments (qv), 15%; plastics and synthetic products, 15%; and alloys and other uses, 9% (16).

Batteries. Cadmium is used in the negative plates of alkaline secondary (rechargeable) batteries, including nickel–cadmium cells, silver–cadmium cells, and mercury–cadmium cells. Nickel–cadmium batteries are the best known and most important of the three. They can be divided into two types, the larger vented cell and the smaller sealed cell. Vented or open cell batteries are used for engine starting in locomotives, aircraft, and other vehicles, and as a standby electrical supply for aircraft, helicopters, and ships. Electric vehicles, such as golf carts, airport luggage carts, and factory forklift trucks also employ nickel–cadmium batteries for propulsion. Sealed nickel–cadmium batteries find applications in portable electronic appliances and tools, portable telephones, underwater lighting equipment, cameras, calculators, and toys. Batteries are expected to remain the principal market for cadmium for the balance of the twentieth century.

Coating and Plating. Elemental cadmium is used principally as an electroplated coating on fabricated steel and cast-iron parts for corrosion protection (see CORROSION AND CORROSION CONTROL). The advantages of cadmium metal for this purpose are ease of electroplating (qv) and high rate of deposition (high throwing power, ie, ability to deposit uniformly on intricate objects); good corrosion resistance to alkali and salt water; high ductility (parts plated can be stamped or otherwise formed); good solderability; and high retention of silvery-white luster for extended periods (see METALLIC COATINGS).

Cadmium is usually plated from a cyanide bath that consists of an aqueous solution of cadmium oxide (35 g L) and sodium cyanide (75 g L). An additive and a brightener are used to produce smooth, fine-grain deposits. Current density ranges from 1.4 to 3.7 A dm^2, depending on the concentration of cadmium cations in the electrolyte.

Cadmium may also be applied by vacuum deposition, dipping, spraying, or mechanical plating with cadmium powder. The future of the cadmium plating industry depends on its ability to meet tighter wastewater restrictions. Mechanical plating with cadmium powder using glass shot is a substitute for electroplating.

Pigments. Cadmium pigments cover the color range from yellow to orange to red, depending on the ratio of cadmium sulfide *[1306-23-6]* to cadmium selenide *[1306-24-7]* in the pigment. As such pigments are stable at elevated temperatures, they find applications as colorants in ceramics and plastics (see COLORANTS FOR CERAMICS; COLORANTS FOR PLASTICS). The bright colors of cadmium pigments are ideally suited for glasses, ceramic glazes, and vitreous enamels. Many types of thermoplastics and thermoset plastics employ cadmium pigments that withstand processing temperatures up to 400°C.

Plastics and Synthetic Products. To prevent degradation of plastics at elevated processing temperatures, it is necessary to use suitable heat stabilizers. For example, flexible poly(vinyl chloride) (PVC) manifests uncontrolled color development in the absence of stabilizers. Accordingly, cadmium salts of organic acids are typically used in a synergistic combination with corresponding barium salts, in about a 1:3 cadmium:barium ratio, to provide a cost-competitive heat stabilizer for flexible PVC.

Alloys

Cadmium is an important component in brazing and low melting alloys, used in bearings, solders, and nuclear reactor control rods, and as a hardener for

copper (see BEARING MATERIALS). Of interest are two brazing alloys: 20% Ag; 45% Cu; 30% Zn; 5% Cd (mp 615°C; flow point 815°C), and ASTM Ag 2 which is 35% Ag; 26% Cu; 21% Zn; 18% Cd (mp 607°C; flow point 702°C). Other useful brazing compositions are also available (22,23) (see SOLDERS AND BRAZING FILLER MATERIALS).

The commonly used low melting or fusible cadmium alloys are AsarcoLo 158 or Cerrobend (50% Bi; 26.7% Pb; 13.3% Sn; 10% Cd; mp 70°C) for bending pipes and thin sections, glass lens grinding blocks, and fire protection devices; AsarcoLo 158-190 or Cerrosafe (42.5% Bi; 37.7% Pb; 11.3% Sn; 8.5% Cd; mp 70–87°C) for foundry patterns, spotting fixtures, solder, and proofcasting molds; and AsarcoLo 117 or Cerrelow 117 (44.7% Bi; 22.6% Pb; 8.3% Sn; 5.3% Cd; 19.1% In; mp 47°C) for fusible cores, soldering and sealing, holding irregular pieces for machining and plastic lens grinding blocks. Other low melting alloys (24) are listed in Table 3.

Table 3. Low Melting Cadmium Alloys

	Composition, wt %					
System	Bi	Cd	In	Sn	Pb	Mp, °C
Sn–Pb–Cd		18		51	31	145
Bi–Cd	60	40				144
Cd–In		25	75			123
Bi–Cd–Sn	54	20		26		103
In–Cd–Sn		14	44	42		93
Bi–Cd–Pb	52	8			40	92
In–Bi–Cd	30	8	62			62

For soldering aluminum, combinations of cadmium and zinc are widely used, the most satisfactory being the 60% Cd–40% Zn alloy, in addition to a 95% Cd–5% Ag solder. In high speed and high temperature applications, which are too severe for tin or lead bearings, SAE 18, containing 1% nickel and 99% cadmium, and SAE 180, containing 0.7% silver, 0.6% copper, and 98.7% cadmium, are employed.

Additions of cadmium (0.05–1.3%) to copper raise the recrystallization temperature and improve the mechanical properties, especially in cold-worked conditions, with relatively little reduction in conductivity. Copper containing 0.07% cadmium is used in automotive cooling fins, heavy-duty radiators, motor commutators, and electric terminals.

An alloy containing 80% Ag, 15% In, and 5% Cd is used in control rods in nuclear reactors because it has a high neutron cross-section and good mechanical strength (see NUCLEAR REACTORS).

Silver containing 2.5–15% cadmium oxide is used extensively for producing electrical contacts (see ELECTRICAL CONNECTORS).

The intermetallic compounds with Group 16 (VIA) elements including CdS, CdSe, and CdTe have interesting semiconductor properties for photoconductors, photovoltaic cells, and ir windows. Cadmium sulfide is widely used as a phosphor in television tubes.

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CADMIUM COMPOUNDS

Naturally occurring cadmium compounds are limited to the rare minerals, greenockite *[1317-58-4]*, CdS, and otavite (1), an oxycarbonate, but neither is an economically important source of cadmium metal or its compounds. Instead, cadmium compounds are more usually derived from metallic cadmium *[7440-43-9]* which is produced as a by-product of lead–zinc smelting or electrolysis (see CADMIUM AND CADMIUM ALLOYS). Typically, this cadmium metal is burnt as a vapor, to produce the brown-black cadmium oxide *[1306-19-0]*, CdO, which then acts as a convenient starting material for most of the economically important compounds.

Properties

Cadmium is a member of Group 12 (Zn, Cd, Hg) of the Periodic Table, having a filled *d* shell of electrons $4d^{10}5s^2$ which dictates the usual valence state of +2. In rare instances the +1 oxidation state may be produced in the form of dimeric Cd_2^{2+} species *[59458-73-0]*, eg, as dark red melts of Cd^0 dissolved in molten cadmium halides or as diamagnetic yellow solids such as $(Cd_2)^{2+}(AlCl_4)_2$ *[79110-87-5]* (2). The Cd_2^{2+} species is unstable in water or other donor solvents, immediately disproportionating to Cd^{2+} and Cd. In general, cadmium compounds exhibit properties similar to the corresponding zinc compounds. Compounds and properties are listed in Table 1. Cadmium(II) *[22537-48-0]* tends to favor tetrahedral coordination in its compounds, particularly in solution as complexes, eg, tetraamminecadmium(II) *[18373-05-2]*, $Cd(NH_3)_4^{2+}$. However, solid-state cadmium-containing oxide or halide materials frequently exhibit octahedral coordination at the Cd^{2+} ion, eg, the rock-salt structure found for CdO.

Table 1. Physical and Chemical Properties of Selected Cadmium Compounds[a]

Compound	CAS Registry Number	$\Delta H^\circ_{f,298}$, kJ/mol[b]	$\Delta G^\circ_{f,298}$, kJ/mol[b]	S°_{298}, J/mol·K[b]	Density, g/mL	C°_p, J/mol·K[b]	Mp, °C	ΔH_{fus}, kJ/mol[b]	Aqueous solubility, g/100 g H_2O[c]	Crystal[d] structure	Unit cell dimensions, nm
cadmium anti-monide CdSb	*[12050-27-0]*	14.4	13.0	92.9	6.92		452	32.05		ortho–rhomb	a = 0.6471 b = 0.8253 c = 8.526
cadmium bromide $CdBr_2$	*[7789-42-6]*	316	296	137.2	5.192	76.7	568	20.92	95_{18}	hex	a = 0.395 c = 1.867
cadmium carbonate $CdCO_3$	*[513-78-0]*	751	669	92.5	4.26		332 dec		2.8×10^{-6}	rhomb	a = 0.61306
cadmium chloride $CdCl_2$	*[10108-64-2]*	391	344	115.3	4.05	74.7	568	22.176	128.6_{30}	hex	a = 0.3854 c = 1.746
cadmium fluoride CdF_2	*[7790-79-6]*	700	648	77.4	6.39		1048	22.594	3.45_{25}	cubic	a = 0.53880
cadmium hydroxide $Cd(OH)_2$	*[21041-95-2]*	561	474	96.2	4.79		150 dec		2.6×10^{-4}	hex	a = 0.3475 c = 0.467
cadmium iodide CdI_2, α-form	*[7790-80-9]*	203	201	161.1	5.67	80.0	387	33.472	86_{25}	hex	a = 0.424 c = 0.684
										(hex)[e]	(c = 1.367)[e]
cadmium nitrate $Cd(NO_3)_2$	*[10325-94-7]*	456	255	197.9			350		109_0	cubic	a = 0.756
cadmium nitrate tetrahydrate $Cd(NO_3)_2 \cdot 4H_2O$	*[10022-68-1]*	1649			2.455		59.4	32.636	215_0	ortho–rhomb	a = 0.583 b = 2.575 c = 1.099
cadmium oxide CdO	*[1306-19-0]*	258	228	54.8	8.2	43.4	1540 sub	243.509 sub	9.6×10^{-4}	cubic	a = 0.46953
cadmium	*[1306-24-7]*	136	100	96.2	5.81		1350	305.3		hex (cubic)[e]	a = 0.4309 c = 0.7021

selenide CdSe, α-form							dissoc	07 dissoc			
											(a = 0.605)[e]
	[13477-19-5]	1189	1105	97.5	4.928	88.6	1242			monoclinic	a = 1.504
cadmium *m*-silicate $CdSiO_3$											b = 0.710
											c = 0.696
	[10124-36-4]	933	823	123.0	4.691	99.6	1000	20.084	76.6_{20}	ortho–rhomb	a = 0.4717
cadmium sulfate $CdSO_4$											b = 0.6559
											c = 0.4701
	[13477-20-8]	1240	1069	154.0	3.79	134.6				monoclinic	a = 7.607
							105 trans				b = 0.7541
cadmium sulfate hydrate $CdSO_4 \cdot H_2O$											c = 8.186
	[7790-89-3]	1729	1465	229.6	3.09	213.3			113_0	monoclinic	a = 0.947
							80 trans				b = 1.184
cadmium sulfate hydrate $3CdSO_4 \cdot 8H_2O$											c = 1.635
	[1306-23-6]	162	156	64.9					$1.3 \times 10_{18}^{4}$	hex	a = 0.41348
cadmium sulfide CdS, α-form					4.82 (4.50)[e]		980 sub in N_2	201.669 subl			c = 0.6749
	[1306-25-8]	92	92	100.4	6.20		1045			(cubic)[e]	(a = 0.5818)[e]
cadmium telluride CdTe										hex	a = 0.457
											c = 0.747
										(cubic)[e]	(a = 0.6480)[e]

[a] Refs. 3–12.

[b] To convert J to cal, divide by 4.184.

[c] Subscript denotes temperature in °C.

[d] Ortho–rhomb is orthorhombic and hex is hexagonal.

[e] β-form.

Economic Aspects

Primary cadmium prices rose sharply in 1987–1988, from $3.60 to $15.50 kg in 1–5 metric ton lots (13), largely as a result of speculative stockpiling and strong demand driven by rapid growth in the Ni–Cd storage battery market. Prices decreased just as sharply in 1990–1991 however, reaching ~$3.15 kg in late 1990, as a result of erosion of consumer stockpiles, regulatory pressures, and a slow-down in the Ni–Cd battery market (14,15).

Uses

The principal areas of cadmium usage in terms of U.S. consumption in 1990 were batteries (qv), 50%; pigments (qv), 20%; plastic stabilizers, 15%; metal finishing, 10%; electronics and optics, <5%; and catalysts (qv), <5% (14–17).

Cadmium hydroxide is the anode material of Ag–Cd and Ni–Cd rechargeable storage batteries (see BATTERIES, SECONDARY CELLS). Cadmium sulfide, selenide, and especially telluride find utility in solar cells (see SOLAR ENERGY). Cadmium sulfide, lithopone, and sulfoselenide are used as colorants (orange, yellow, red) for plastics, glass, glazes, rubber, and fireworks (see COLORANTS FOR CERAMICS; COLORANTS FOR PLASTICS; PIGMENTS).

In flexible PVC, cadmium salts of long-chain organic acids, such as stearate and laurate, are used in combination with similary Ba^{2+} salts as heat and light stabilizers (see HEAT STABILIZERS). Cadmium cyanide, acetate, fluoroborate, or sulfate is used as an electrolyte in coating a thin cadmium layer, ie, electroplating (qv), onto other metals thereby imparting enhanced corrosion protection. Cadmium protective overlayers are also deposited by mechanical plating or vapor deposition (see METALLIC COATINGS).

The cadmium chalcogenide semiconductors (qv) have found numerous applications ranging from rectifiers to photoconductive detectors in smoke alarms. Many Cd compounds, eg, sulfide, tungstate, selenide, telluride, and oxide, are used as phosphors in luminescent screens and scintillation counters. Glass colored with cadmium sulfoselenides is used as a color filter in spectroscopy and has recently attracted attention as a third-order, nonlinear optical switching material (see NONLINEAR OPTICAL MATERIALS). Dialkylcadmium compounds are polymerization catalysts for production of poly(vinyl chloride) (PVC), poly(vinyl acetate) (PVA), and poly(methyl methacrylate) (PMMA). Mixed with $TiCl_4$, they catalyze the polymerization of ethylene and propylene.

Demand for cadmium and its compounds in the United States has generally declined after peaking in the 7000–8000 t yr range during the late 1970s (14,15). Apparent consumption was 3107 metric tons in 1990. World refinery production during the 1980s remained roughly constant at ~19,500 t yr (15). The declining use of cadmium in plastics and as pigments in the 1980s, largely because of health and environmental concerns and the concomitant introduction of Cd substitutes, has been offset by its increased use in rechargeable storage (Ni–Cd) batteries. Continued and growing concern over the toxicity of cadmium in the environment is expected to lead to alternatives for cadmium compounds in all applications. The outlook for cadmium use, therefore, seems stable throughout the 1990s (14).

Analysis

Because of the increasing emphasis on monitoring of environmental cadmium the determination of extremely low concentrations of cadmium ion has been developed. Table 2 lists the most prevalent analytical techniques and the detection limits. In general, for soluble cadmium species, atomic absorption is the method of choice for detection of very low concentrations. Mobile prompt gamma *in vivo* activation analysis has been developed for the nondestructive sampling of cadmium in biological samples (18).

Table 2. Analytical Methods and Detection Limits for Cadmium Ion[a]

Method	Detection limit, ppb
atomic absorption spectroscopy (graphite furnace)	0.008
polarography (square wave)	10
x-ray fluorescence (energy dispersive)	5000
neutron activation analysis	1
isotope dilution	10
inductively coupled plasma emission spectra	1

[a] Ref. 19.

At higher levels, cadmium may be estimated gravimetrically following precipitation with sulfide (20), β-naphthoquinoline (21), or after plating from a cyanide-containing solution onto a stationary platinum cathode. Volumetric procedures rely on preliminary precipitation of the sulfide that is purified and then dissolved in acid whereupon the liberated H_2S may be titrated with iodine. An alternative, should zinc be a likely contaminant, is to precipitate with diethyldithiocarbamate and then to redissolve in acid and titrate with sodium ethylenetriaminetetraacetate (EDTA) using Eriochrome Black T as indicator (22).

Toxicity and Environmental Aspects

Cadmium, both as the free metal and in its compounds, is highly toxic and has been designated one of the 100 most hazardous substances under Section 110 of the Superfund Amendments and Reauthorization Act of 1986 (15). Poisoning may occur either via inhalation or ingestion. Only about 6% of the estimated 40–50 μg/d of ingested cadmium is absorbed by the body, whereas 25–50% of the 2–10 μg/d of cadmium in inhaled dust is absorbed (19,23). Cadmium is present in cigarette smoke and as much as 0.1–0.2 micrograms per cigarette may be absorbed by the lungs (24).

Chemical pneumonitis or pulmonary edema may result from acute exposure to cadmium fumes, as oxide or chloride aerosols, at a dose of 5 mg/m^3 over an 8-h period. One mg/m^3 inhaled over the same time period gives rise to clinically evident symptoms in sensitive individuals. Deaths from acute cadmium poisoning have resulted from inhalation of cadmium oxide smokes and fumes, usually from welding operations on cadmium plated steels in poorly ventilated areas. Acute ingestion of cadmium concentrations above ~15 ppm (0.1–1.0 mg/(kg·d)) produce symptoms of nausea, vomiting, abdominal cramps, and headache (25). Possible sources of such poisoning have been traced to cadmium-plated cooking utensils, cadmium solders in water coolers, or from acid juices stored in ceramic pots glazed using cadmium-containing compounds. Current atmospheric time-weighted average (TWA) permissible exposure limits (PEL) are 200 μg/m^3 (dust) or 100 μg/m^3 (oxide fumes) in an 8-h workday (25). OSHA, in February 1990, proposed (14) a new PEL level of either 5 or 1 μg/m^3 for all forms of airborne cadmium and as of this writing this standard is under review. Acceptable OSHA 15-min ceiling concentrations are 600 μg/m^3 for dusts and 300 μg/m^3 for oxide fumes (25). The maximum for dissolved Cd in drinking water recommended by WHO is 5 μg/L (15,25).

Cadmium is efficiently scavenged by the body and biological half-times for cadmium excretion are on the order of 10–30 years. The kidneys and liver appear to be the organs of concentration for cadmium; kidney damage leading to proteinuria is probably the most common manifestation of chronic cadmium exposure. The combination of dietary deficiency and high cadmium exposure resulted in the most infamous example of suspected cadmium poisoning on record where a disease known as itai-itai afflicted elderly Japanese women from the Zinzu river basin after World War II. Whereas the role of cadmium in the disease is still controversial, it seems clear that the severe weakening of bone tissue associated with the disease was a result of demineralization induced by cadmium (19). Although there is some evidence that cadmium may be carcinogenic in animals under certain exposure conditions, the association between cadmium exposure and cancer in humans remains tenuous. The increased risk of prostatic cancer in workers exposed to cadmium dusts and fumes has been reported to be significant, but the number of cases reported so far is very small (26) and the conclusions have been questioned. More recent data have described a possible link between cadmium exposure and lung cancer in humans (25). In 1989 the EPA denied a petition requesting removal of CdS and CdSe from their list of toxic chemicals, citing available cancer data on CdS and other cadmium compounds (27). EPA maintains that cadmium is a probable human carcinogen (Group B1) but only by the inhalation route.

Cadmium discharges to air and water are decreasing as primary zinc producers have largely converted to electrolytic processing and as more efficient pollution control technologies take effect (28). Most of the cadmium released to the environment is now in the form of solid wastes such as coal ash, sewage sludge (5–20 ppm), flue dust, and fertilizers (2–20 ppm). Effluent limits of all sources have been strictly regulated in recent years and cadmium emissions are controlled by the best available technology including membrane filtration (see EXHAUST CONTROL, INDUSTRIAL). Recycling programs have been instituted by several battery manufacturers, eg, in France, Belgium, Japan, Sweden, and Korea (15), aimed at reducing cadmium pollution from spent Ni–Cd batteries.

Inorganic Compounds

Cadmium Arsenides, Antimonides, and Phosphides. Cadmium arsenide *[12511-93-2]*, CdAs, cadmium diarsenide *[12044-40-5]*, $CdAs_2$, and tricadmium diarsenide *[12006-15-4]*, Cd_3As_2, are known. Cd_3As_2 is prepared as grey tetragonal crystals, a = 0.8945 nm, c = 1.265 nm; d = 6.25 g/mL; mp 721°C (4,7); $\Delta H^{\circ}_{f,298}$ = −41.84 kJ/mol (−10 kcal/mol) (3) by heating stoichiometric amounts of the elements to fusion in an argon atmosphere. It is an *n*-type semiconductor having high electron mobility (10,000 cm^2/V·s), electron concentration of 3 × 10^{18} cm^{-3} and a band gap energy of 0.13 *e*V. It may also be prepared by wet chemical methods involving passage of arsine gas through a weakly ammoniacal solution of cadmium sulfate. The fine black precipitate liberates arsine when treated with acid and inflames upon treatment with oxidants. Thin films (qv) of Cd_3As_2 find application as ultrasonic multipliers, photodetectors, thermodetectors, and Hall generators (29). Reagent-grade material sells for $4.00/g in small lots. $CdAs_2$ is prepared by slow heating, to 700°C, of stoichiometric amounts of the elements in a sealed, evacuated, quartz ampul. The grey tetragonal crystals, a = 0.465 nm; c = 0.793 nm; d = 5.80 g/mL; mp 621°C; $\Delta H^{\circ}_{f,298}$ = −17.5 kJ/mol (−4.18 kcal/mol) (3), decompose upon heating to give arsenic and Cd_3As_2. The additional, less well characterized phase, CdAs, has been prepared by decomposition of $CdAs_2$ at high pressure to give orthorhombic grey crystals, a = 0.5993 nm, b = 0.7819 nm, c = 0.8011 nm; d = 6.63 g/mL; which decomposes instead of melting (30).

Antimonides of formulas CdSb and Cd_3Sb_2 have been reported. Both are usually prepared by direct union of the elements, the former is a hole-type semiconductor (9), with properties shown in Table 1, and finds use as a thermoelectric generator. Reagent-grade material costs $2.00/g in small lots. The band gap energy is 0.46 *e*V (2.70 μm) (31); ΔH_{vap} is 138 kJ/mol (33.0 kcal/mol). Dicadmium triantimonide *[12014-29-8]*, Cd_2Sb_3, is a metastable, white crystalline compound of monoclinic symmetry: a = 0.72 nm, b = 1.351 nm, c = 0.616 nm, β = 100°14′; d = 7.014 g/mL; mp 423°C (7).

The phosphides tricadmium diphosphide *[12014-28-7]*, Cd_3P_2, cadmium diphosphide *[12133-44-7]*, CdP_2, and cadmium tetraphosphide *[12050-26-9]*, CdP_4, may all be prepared by indirect fusion of the elements, usually by passing phosphorus vapors, in a nitrogen or hydrogen carrier gas,

over heated cadmium. Cd_3P_2 forms grey metallic needles of tetragonal symmetry, a 0.894 nm, c 1.228 nm; d 5.95 g mL; mp 700°C (4,7). It may also be prepared by passage of phosphine gas through a solution of cadmium ion and, if a surfactant such as polyphosphate is present, may be maintained in solution as a size-quantized semiconductor colloid the color of which ranges from pale yellow to black, dependent on particle size (32). It is an *n*-type semiconductor with near metallic mobilities (31) and was the first $A_3(II)B_2$ (31) compound to show laser action (29). CdP_2 may be prepared by heating a mixture of ammonium phosphate, cadmium carbonate, and carbon black and has a structure consisting of *P* chains where each *P* atom is bonded to two other *P* atoms and two Cd atoms. CdP_4 has the Cd atoms in octahedral coordination sandwiched between layers of *P* atoms (33).

Cadmium Borates. Of general formula $nCdO{\cdot}mB_2O_3$, the cadmium borates are prepared from $CdO{-}B_2O_3$ melts (7) and are used as phosphors. Materials $n = 1$, $m = 3$ *[20571-45-3]*; n 2, m 3, and $n = 3$, $m = 1$, all show green cathodoluminescence. Mn-doped material with n 2, m 1 luminesces strongly orange in electromagnetic radiation. Cadmium borotungstate *[1306-26-9]*, $2CdO{\cdot}B_2O_3{\cdot}WO_3{\cdot}18H_2O$, solutions can have densities up to 3.28 g mL and have utility as flotation (qv) media for mineral separations. Cadmium fluoroborate *[14486-19-2]*, $Cd(BF_4)_2$, is very hygroscopic and is used to prepare electroplating baths for high strength steels where the normal cyanide baths cause problems of hydrogen embrittlement. A 44% solution sells for $36 kg of contained Cd.

Cadmium Carbonate. Pure cadmium carbonate, as the hemihydrate, $CdCO_3{\cdot}\frac{1}{2}H_2O$, is obtained only when ammonium carbonate is used to precipitate the white, prismatic crystals from cadmium ion solutions; alkali carbonates precipitate the oxycarbonate. The carbonate is also produced by heating an acidified solution of cadmium chloride and urea in a sealed tube at 200°C (7). Cadmium oxide also slowly absorbs carbon dioxide to form the normal carbonate. The decomposition $CdCO_3 \rightarrow CdO + CO_2$ gives a CO_2 partial pressure of 101 kPa (1 atm) at 357°C. The carbonate eliminates CO_2 in acids and acts as a convenient source of other Cd compounds in this type of reaction. It is soluble, because of complex ion formation, in ammonium ion- or cyanide ion-containing solutions. The carbonate is used as a catalyst in organic chemistry and reagent-grade material sells for $63 kg.

Cadmium Complexes. Aqueous cadmium ion complexes are listed in Table 3. Cadmium binds four or less anionic ligands in solution generally resulting in colorless complexes. Many organic ligands form complexes with cadmium ion, the more common being methylamine, thiourea, oxalic acid, tartaric acid, dimethylglyoxime, pyridine, acetic acid, ethylenediamine tetraacetic acid, thiols, and glycolic acid. Stability constants are provided in the literature (34).

Table 3. Thermodynamic and Stability Constant Data for Selected Aqueous Cadmium Complexes[a,b]

Complex ion	CAS Registry Number	$\Delta H°_{f298}$ kJ mol[c]	$\Delta G°_{f298}$ kJ mol[c]	Stability constant
$CdCl^+$	*[14457-58-0]*	240.5	224.4	$\log K_1$ 1.32
$CdCl_3^-$	*[21439-35-0]*	561.0	487.0	$\log K_3$ 0.09
$Cd(CN)^{2-}_4$	*[16041-14-8]*	428.0	507.5	$\log K_4$ 3.58
$Cd(NH_3)^{2+}_2$	*[47942-20-1]*	266.1	159.0	$\log K_2$ 2.24
$Cd(NH_3)^{2+}_4$	*[18373-05-2]*	450.2	226.4	$\log K_4$ 1.18
$CdBr^+$	*[15691-37-9]*	200.8	193.9	$\log K_1$ 1.97
$CdBr_3^-$	*[21439-36-1]*		407.5	$\log K_3$ 0.24
CdI^+	*[15691-38-0]*	141.0	141.4	$\log K_1$ 2.08
CdI_3^-	*[15691-42-6]*		259.4	$\log K_3$ 2.09
CdI^{2-}_4	*[15975-72-1]*	341.8	315.9	$\log K_4$ 1.59
$CdSCN^+$	*[18194-99-5]*		7.5	$\log K_1$ 1.90
$Cd(SCN)^{2-}_4$	*[19438-35-8]*			$\log K_4$ ca 0.1
$Cd(N_3)^{2-}_4$	*[16408-27-8]*		1,295.0	$\log K_4$ 0.76

[a] Standard state M 1.

[b] Refs. 3 and 34.

[c] To convert kJ to kcal, divide by 4.184.

Cadmium complexes are of importance to the electroplating industry because baths containing complexed cadmium have excellent covering power and yield dense, fine grains. The complexed cation permits high cathodic overvoltages and this changed deposition potential allows codeposition of other metals. In commercial operation the cyanide-plating bath, containing the complex ion $Cd(CN)^{2-}_4$ and formed from CdO (24 g L), Cd metal (25 g L), and NaCN (105 g L), is the bath of choice. The exception is for high strength steels, which suffer embrittlement as a result of hydrogen incorporation, or in areas where cyanide effluent control is particularly difficult. In such cases the fluoroborate bath is the usual alternative although other electrolytes such as sulfate, sulfamate, chloride, and pyrophosphate have been used.

Cadmium Halides. Cadmium halides show a steadily increasing covalency of the metal–halide bond proceeding from fluoride through to iodide. Bond lengths increase through the series: F, 0.197 nm; Cl, 0.221 nm; Br, 0.237 nm; I, 0.255 nm. The fluoride is much less soluble in water than the others (see Table 1) and the Cl, Br, and I compounds dissolve to a significant extent in alcohols, ethers, acetone, and liquid ammonia. Boiling points and corresponding ΔH_{vap}'s are CdF_2, 1747°C, 234 kJ mol (55.9 kcal mol); $CdCl_2$, 960°C, 125 kJ mol (29.9 kcal mol); $CdBr_2$, 963°C, 113 kJ mol (27.0 kcal mol); and CdI_2, 787°C, 106 kJ mol (25.3 kcal mol).

Aqueous solutions have low conductivities resulting from extensive complex ion formation. The halides, along with the chalcogenides, are sometimes used in pyrotechnics to give blue flames and as catalysts for a number of organic reactions.

Cadmium Fluoride. Elemental fluorine reacts with cadmium metal as well as the oxide, sulfide, and chloride to give CdF_2 *[7790-79-6]*. Alternatively, treatment of $CdCO_3$ with 40% HF yields a solution of CdF_2, which may be evaporated to recover efflorescent crystals of the dihydrate. CdF_2 has been used in phosphors, glass manufacture, nuclear reactor controls, and electric brushes and in 1991 sold as a pure electronic grade (99.99%) at $1 g.

Cadmium Chloride. Data for anhydrous material are listed in Table 1 but cadmium chloride also exists as hydrates having 1, 2, 2.5, and 4 molecules of water per formula unit, all of which are efflorescent in dry air. The pentahydrate $2CdCl_2{\cdot}5H_2O$ *[7790-78-5]* is the most normal commercial form of the chloride and exists as colorless crystals of $d = 3.33$ g mL; $\Delta H_{f,298}$ 1132 kJ mol (270.6 kcal mol) (3). It may be prepared by dissolving the metal, the carbonate, oxide, sulfide, or hydroxide in hydrochloric acid and evaporating the solution. Anhydrous material may be derived from this by heating in a stream of dry HCl. The pentahydrate is sold for $38 kg (technical-grade) in 45 kg lots and has been used in photography, photocopying, dyeing, and calico printing (with thiosulfate), vacuum tube manufacture, cadmium pigment manufacture, galvanoplasty, lubricants, ice-nucleation agents, and in the manufacture of special mirrors.

Cadmium Bromide. The hydrated bromide is prepared by dissolution of cadmium carbonate, oxide, sulfide, or hydroxide in hydrobromic acid. The white crystalline material is cadmium bromide tetrahydrate *[13464-92-1]*, $CdBr_2{\cdot}4H_2O$, $\Delta H_{f,298}$ 1492.55 kJ mol (356.73 kcal mol) (3) which dehydrates to the monohydrate at 36°C and to the yellow, anhydrous material $CdBr_2$ at 200°C. The anhydrous material may be prepared directly from the elements at elevated temperature or from anhydrous cadmium acetate *[543-90-8]*, $Cd(CH_3COO)_2$, mixed with glacial acetic acid and acetyl bromide. Uses include photography, process engraving, and lithography and small lots of reagent-grade material may be purchased for $425 kg.

Cadmium Iodide. Two crystal morphologies exist for CdI_2 *[7790-80-9]*, the white α-form (see Table 1) and the brown β-form. The latter crystallizes from fused-salt mixtures. The more common α-form has a saltlike layered crystal structure where individual layer sheets contact each other through van der Waals' interactions of the outer iodide ions (33). This structure dictates the highly lamellar and easily cleaved nature of CdI_2 crystals. CdI_2 is prepared either by direct combination of the elements in the absence of oxygen or by the dissolution of cadmium metal, the oxide, carbonate, hydroxide, or sulfide in hydroiodic acid. Precipitation of CdI_2 from a solution of the sulfate using KI also yields the hexagonal, lamellar, lustrous crystals of the α-form. The iodide is used in electro-deposition of Cd, as a nematocide, in phosphors, lubricants, photoconductors, in photography, process engraving, and lithography (qv). The material is sold in small lots at reagent-grade for $352 kg.

Cadmium Hydroxide. $Cd(OH)_2$ *[21041-95-2]* is best prepared by addition of cadmium nitrate solution to a boiling solution of sodium or potassium hydroxide. The crystals adopt the layered structure of CdI_2: there is contact between hydroxide ions of adjacent layers. $Cd(OH)_2$ can be dehydrated to the oxide by gentle heating to 200°C; it absorbs CO_2 from the air forming the basic carbonate. It is soluble in dilute acids and solutions of ammonium ions, ferric chloride, alkali halides, cyanides, and thiocyanates forming complex ions.

$Cd(OH)_2$ is much more basic than $Zn(OH)_2$ and is soluble in 5 *N* NaOH at 1.3 g L as the anionic complex tetrahydroxocadmate *[26214-93-7]*, $Cd(OH)^2{}_4$. Technical-grade $Cd(OH)_2$ sold for $74 kg in 1991 and its most important utility is as the active anode in rechargeable Ni–Cd and Ag–Cd storage batteries. The chemical reaction responsible for the charge–discharge of the batteries is (35):

$$Cd(OH)_2 + 2\,Ni(OH)_2 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Cd + 2\,NiOOH + 2\,H_2O$$

These batteries account for ~50% of 1990 U.S. annual consumption of cadmium and are used in heavy-duty, long-life applications such as rechargeable tools, appliances, instruments, and electronics (36).

Cadmium Nitrate. Anhydrous $Cd(NO_3)_2$ *[10325-94-7]* is obtained by action of nitric acid on the carbonate to give cadmium nitrate tetrahydrate *[10022-68-1]* by crystallization; this may then be dried by careful exposure to concentrated nitric acid at 20°C. The tetrahydrate, bp 132°C, is soluble in alcohols, acetone, and ethyl acetate and most polar organic solvents.

Cadmium nitrate is the preferred starting material for $Cd(OH)_2$ for use as the anode in alkaline batteries. The sintered anode matrix of such batteries is saturated with cadmium nitrate (480–500 g L Cd) and cadmium hydroxide is formed therein by standardized electrolysis and drying (37). The tetrahydrate sells for $29.10 kg in 20 kg lots. Other uses include photographic emulsions and as a colorant in glass and ceramics.

Cadmium Oxide. Cadmium vapor burns in air to produce the dark brown oxide CdO *[1306-19-0]* and the commercial process for its production is as follows. Pure Cd metal is melted and then vaporized whereupon air is blown through the hot vapor, oxidizing the cadmium and carrying the product to a baghouse. The resultant oxide (particle size controlled by the air–Cd ratio) is calcined at 550°C to ensure uniform properties. Other preparative approaches include calcination of the carbonate, nitrate, sulfate, or hydroxide in air; oxidation of the sulfide by heating in air and by pyrolysis of cadmium formate *[4464-23-7]* or cadmium oxalate *[814-88-0]*. These last two methods give very finely divided material of high activity. Oxide smokes of extreme toxicity may be produced by spontaneous combustion of the cadmium alkyls, eg, $Cd(CH_3)_2$, in air. CdO has the rock-salt crystal structure with octahedral coordination at the Cd and O ions. Cadmium peroxide *[12139-22-9]*, CdO_2, has been reported and is also cubic having a 0.5313 nm and d 6.396 g mL.

CdO is soluble in dilute acids but not in water or alkalies and forms a variety of soluble complexes, the most important being with sodium cyanide in the bath used in electroplating. CdO is an *n*-type semiconductor of band gap energy 222 kJ mol (53.1 kcal mol). It may be reduced to the metal with hydrogen, carbon, or carbon monoxide at 600°C. It sells for $36 kg and finds uses as a starting material for PVC heat stabilizers and other inorganic Cd compounds and as the cadmium source in cyanide plating baths. Ag–CdO contacts are used in electrical devices whereas high purity CdO is used as a second depolarizer, along with Ag_2O, in Ag–Zn storage batteries (38). CdO is also used in nitrile rubbers and plastics such as Teflon where it improves high temperature properties and heat resistance. Its use as a high temperature resistor material takes advantage of its low specific resistivity and low negative temperature coefficient of resistivity. Other uses include in phosphors, as a glass colorant, as a nematocide, as an ascaricide or anthelmintic in swine, and as a catalyst of a variety of organic chemical reactions.

Cadmium Phosphates. Cadmium phosphate *[13477-17-3]*, $Cd_3(PO_4)_2$, is prepared by reaction of cadmium nitrate with potassium dihydrogen phosphate in the presence of sodium hydroxide to neutralize the KH_2PO_4 (7). This material is both a catalyst and a phosphor. Cadmium dihydrogen phosphate *[17695-54-4]*, $Cd(H_2PO_4)_2$, is prepared by adding phosphoric acid to a slurry of cadmium carbonate in water and acts as a catalyst for the polymerization of gaseous olefins (39). Roasting the dihydrogen compound to 300°C leads to cadmium metaphosphate *[14466-83-2]*, $Cd(PO_3)_2$, which finds utility as an exceptionally bright and stable phosphor.

Cadmium Selenide and Telluride. Both materials are *n*-type semiconductors having band gap energies of 1.74 *e*V (712 nm) for CdSe *[1306-24-7]* and 1.45 *e*V (855 nm) for CdTe *[1306-25-8]* (40). They are best prepared by direct reaction of the elements at elevated temperatures in evacuated, sealed quartz tubes. However, the materials may also be prepared by simple wet chemical techniques whereby a solution of cadmium ion is exposed to H_2Se or H_2Te gases in an inert atmosphere or to solutions of the alkali metal selenide or telluride. The heavy precipitates can vary in color from yellow-orange to deep red-black, depending on the particle size of the compound, and this is a manifestation of the size-quantization phenomenon (32) which is particularly well demonstrated by the cadmium chalcogenides. Colloidal suspensions of the semiconductors may be maintained by addition of a surfactant (polyphosphate or micelle-forming agent) to the precipitating solution and such solutions of nanoparticulates have been under intense investigation as nonlinear optical media (32) (see NONLINEAR OPTICAL MATERIALS).

CdSe forms solid solutions with CdS which are used as pigments ranging in color from orange to deep maroon and are called cadmium sulfoselenides. Other uses are in photocells, rectifiers, luminous paints, and as a ruby colorant for glass manufacture. CdSe currently sells for $1.50 g as phosphor-grade (99.999% purity) material.

CdTe is used in infrared optics (41), phosphors, elelctroluminescent devices, photocells, and as a detector for nuclear radiation (42).

Cadmium Silicates. Cadmium orthosilicate *[15857-59-2]*, Cd_2SiO_4, (mp 1246°C; d = 5.83 g mL) and cadmium metasilicate *[13477-19-5]*, $CdSiO_3$, are both prepared by direct reaction of CdO and SiO_2 at 390°C under 30.4 MPa (300 atm) or at 900°C and atmospheric pressure in steam. The materials are phosphors when activated with Mn(II) ion and are both fluorescent and phosphorescent.

Cadmium Sulfate. $CdSO_4 \cdot \frac{8}{3}H_2O$ *[7790-84-3]* is the normal form of cadmium sulfate and is prepared by crystallization of solutions made by dissolving cadmium metal, oxide, sulfide, hydroxide, or carbonate in sulfuric acid. Alternatively, the $\frac{8}{3}$ hydrate is precipitated from such solutions with alcohol. It currently sells for $60 kg as reagent-grade in small lots. The monohydrate *[13577-20-8]* may be prepared by dehydrating this material by heating to 80°C. Anhydrous cadmium sulfate *[10124-36-4]* is prepared by oxidation of the sulfide or sulfite under carefully controlled oxidizing atmospheres at high temperature. An alternative method involves treatment of powdered cadmium nitrate, halides, oxide, or carbonate with dimethyl sulfate (7).

Cadmium sulfate solutions are used in the standard Weston cell and as electrolytes in electroplating as alternatives to cyanide baths. Other uses include phosphors and as a nematocide.

Cadmium Sulfide. CdS *[1306-23-6]* is dimorphic and exists in the sphalerite (cubic) and wurtzite (hexagonal) crystal structures (40). At very high pressures it may exist also as a rock-salt structure type. It is oxidized to the sulfate, basic sulfate, and eventually the oxide on heating in air to 700°C, especially in the presence of moisture (9).

CdS may be prepared ranging in color from white to deep orange-red depending on the preparative method and resultant particle size of the material. The smaller the particle size the lighter the coloration (32) and glass colored with cadmium sulfide is colorless when first cast from the melt where the particle size of the CdS is less than 2 nm. Upon annealing (striking) at 700°C, yellow-orange color develops as the particle size increases as a result of

aggregation in the glass matrix. Direct reaction between H_2S and Cd vapor or between sulfur and cadmium metal or its oxide at high temperature produces CdS. However, a simple method involves treatment of an acidic or neutral cadmium ion solution with H_2S or Na_2S and collection of the dense yellow precipitate is straightforward. At room temperature this method gives yellow solids whereas from boiling solutions one obtains yellow solids at neutral pH but reddish solids at low pH. Acidified cadmium acetate solutions precipitate yellow CdS; ammoniacal solutions give a red modification.

CdS finds its main use as a pigment, particularly in the glass and plastics industry. Production of CdS in the United States is shown (15).

Year	CdS production, t of Cd content
1984	771
1985	477
1986	645
1987	540
1988	345
1989	267
1990	228

Increased concerns over the toxicity and environmental impact of cadmium materials and increased imports of Cd pigments from Europe contributed to the decrease in production in the latter 1980s and 1990s. Pure yellow cadmium sulfides are formulated with red cadmium selenides to form solid solutions called C.P. toners ranging from yellows and oranges (low selenium content) to reds and maroons (high selenide). Such pigments are manufactured on an industrial scale in three steps: (*1*) cadmium sticks are dissolved in sulfuric acid to give a sulfate solution; (*2*) sodium sulfide and selenide are mixed in the desired proportion and added to the cadmium sulfate solution; and (*3*) the precipitated pigment is filtered, washed, dried, and calcined at 700°C in an inert atmosphere to obtain a uniform product.

The cadmium lithopones, ZnS–CdS Se–$BaSO_4$, are additional cadmium sulfide-based pigments prepared by adding barium sulfide to zinc–cadmium sulfate mixtures. Again the colors range from yellow to deep red-maroon depending on additive content. Cadmium pigments in general are very resistant to H_2S, SO_2, light, heat, and other atmospheric conditions and are dense, heavy colorants having good covering power and bright deep shades.

CdS colorants find use in plastics, paints, soaps, rubber, paper, glass, printing inks, ceramic glazes, textiles, and fireworks. Luminescent pigments based on CdS–ZnS are also produced. Pigments based on CdS sell for $35–60 kg. The redder materials are more expensive.

Other uses of CdS take advantage of its semiconducting properties. It is an *n*-type semiconductor with a band gap (wurtzite phase) at 2.58 *e*V (480 nm). It is used as a thin-film cell to convert solar energy to electrical power, is a photoconductor, and is electroluminescent (40). These properties have found use in phosphors, photomultipliers, radiation detectors, thin-film transistors, diodes and rectifiers, electron-beam pumped lasers, and smoke detectors (35). CdS, when shock fractured by pressure release from the cubic phase, has been reported to be a high temperature superconductor having a critical temperature for conversion to the superconductive state in excess of 190 K (43). Finally the nonlinear optical properties of colloidal suspensions of CdS in glass or polymer matrices have been explored as possible light transistors for optical computing applications (32).

Cadmium Tungstate. Cadmium tungstate *[7790-85-4]*, $CdWO_4$, forms white or yellow monoclinic crystals which are highly luminescent, a 0.5029 nm, b 0.5859 nm, c 0.5074 nm; d = 8.033 g mL. It is prepared by the action of tungstic acid on cadmium oxide in a little water (7) and finds use in x-ray screens, scintillation counters, phosphors, and as a catalyst in organic reactions (44). Reagent-grade materials are sold for ~$300 kg in small lots.

Organic Compounds

Many organocadmium compounds are known but few have been of commercial importance. Wanklyn first isolated diethylcadmium in 1856. The properties of this and other dialkylcadmiums are listed in Table 4. In general, these materials are prepared by reaction of an anhydrous cadmium halide with a Grignard or alkyllithium reagent followed by distillation of the volatile material in an inert atmosphere or *in vacuo*. Only the liquid dimethyl compound is reasonably stable and then only when stored in a sealed tube. Dimethylcadmium is mildly pyrophoric in air and produces dense clouds of white, then brown, cadmium oxide smoke, which is highly toxic if breathed (45). When dropped into water, the liquid sinks in large droplets that decompose with a series of small explosive jerks and pops. For this reason, and particularly because of the low thermal stability, most dialkylcadmium materials are prepared and used *in situ* without separation, eg, in the conversion of acid chlorides to speciality ketones (qv):

$$2\,RCOCl + CdR'_2 \rightarrow 2\,RCOR' + CdCl_2$$

Dimethylcadmium has a linear C–Cd–C core with a Cd–C bond length of 0.211 nm (33).

Table 4. Properties of Dialkyl Cadmium Compounds

Compound	CAS Registry Number	Molecular formula	Mp, °C	Bp, °C[a]	Density, g mL
dimethylcadmium	*[506-82-1]*	$(CH_3)_2Cd$	4.5	105.5 (101.3)	1.9846
diethylcadmium	*[592-02-9]*	$(C_2H_5)_2Cd$	21	64 (2.6)	1.6564
dipropylcadmium	*[5905-48-6]*	$(C_3H_7)_2Cd$	83	84 (2.8)	1.4184
dibutylcadmium	*[3431-67-2]*	$(C_4H_9)_2Cd$	48	103.5 (1.6)	1.3054
diisobutylcadmium	*[3431-67-2]*	$(C_4H_9)_2Cd$	37	90.5 (2.6)	1.2674
diisoamylcadmium	*[35061-27-9]*	$(C_5H_{11})_2Cd$	115	121.5 (2.0)	1.2184

[a] Pressure of bp determination is given in kPa in parentheses. To convert kPa to mm Hg, multiply by 7.5.

Many dialkyl and diaryl cadmium compounds have found use as polymerization catalysts. For example, the diethyl compound catalyzes polymerization of vinyl chloride, vinyl acetate, and methyl methacrylate (45), and when mixed with $TiCl_4$, can be used to produce polyethylene and crystalline polypropylene for filaments, textiles, glues, and coatings (45). With >50% $TiCl_4$, diethyl cadmium polymerizes dienes. Diethyl cadmium may be used as an intermediate ethylating agent in the production of tetraethyllead. The diaryl compounds such as diphenylcadmium *[2674-04-6]*, $(C_6H_5)_2Cd$, (mp 174°C) are also polymerization catalysts. These compounds are also prepared using Grignard or aryllithium reagents in tetrahydrofuran (THF) solvent but may be prepared by direct metal substitution reactions such as:

$$(C_6H_5)_2Hg + Cd \rightarrow (C_6H_5)_2Cd + Hg$$

Dimethylcadmium has found use as a volatile source of Cd for metal organic chemical vapor deposition (MOCVD) production of cadmium-containing semiconductor thin films (qv) such as CdS, $Cd_{1-x}Hg_xTe$, or $Cd_{1-x}Mn_xTe$, as multiple quantum well species (32). Semiconductor-grade material sells for

$21 g.

Cadmium alkyl and aryl halides, RCdX, as well as cadmium allyls have been prepared by Grignard reactions but, as yet, have not realized any commercially important uses despite reactivity toward a number of organic and inorganic materials.

Cadmium Acetate. Cadmium acetate *[543-90-8]*, $Cd(CH_3COO)_2 \cdot nH_2O$, can exist as the anhydrous salt (n 0) mp 256°C, d 2.341 g mL or as one of a series of hydrates (n = 1–3). The anhydrous material may be prepared by treating cadmium nitrate with acetic anhydride or by very careful heating and drying the dihydrate at ~130°C. The cadmium acetate dihydrate *[5743-04-4]*, d 2.01 g mL, is obtained by dissolving cadmium metal or its oxide, hydroxide, or carbonate in acetic acid and crystallizing. Cadmium acetate monohydrate *[543-90-8]* may be obtained from the dihydrate by careful drying. All acetates are very soluble in water and alcohols.

Cadmium acetate is a colorant for glass and textiles, a glaze for ceramics where it produces iridescent effects, a starting material for preparation of the cadmium halides, and is an alternative to the cyanide bath for cadmium electroplating. In 1991, cadmium acetate dihydrate sold for $59.50 kg in 2 kg lots of reagent-grade material.

Organocadmium Soaps. Other salts of organic acids, apart from the acetate, have found wide usage as heat and light stabilizers for plastics, especially flexible PVC. During the molding process, unstabilized PVC begins to lose HCl at 95°C resulting in marked yellowing of the molded article. In addition, the free HCl acts as a catalyst for further degradation of the polymer and the unsaturated polymer chains left behind upon HCl elimination absorb more uv radiation which also breaks down the polymer chains leading to embrittlement. Cadmium salts of long-chain fatty acids such as laurate and stearate, cadmium soaps, are acid acceptors that react with HCl to give the weak organic acid and $CdCl_2$, and so their incorporation into the plastic article prevents early discoloration. However, cadmium chloride is a strong Lewis acid, capable of initiating polymer degradation itself. For this reason, barium compounds of the same fatty acids are used in conjunction with the cadmium stabilizers because there is a rapid exchange of chloride from cadmium to barium. A phosphite chelator is typically added to the mixture to produce an almost complete stabilizer package (35).

The solid soaps are prepared from cadmium chloride solution by precipitation with sodium salts of the fatty acids. Cadmium laurate *[2605-44-9]*, $Cd(C_{12}H_{24}O_2)_2$, cadmium stearate *[2223-93-0]*, $Cd(C_{18}H_{35}O_2)_2$, cadmium palmitate *[6427-86-7]*, $Cd(C_{16}H_{32}O_2)_2$, and cadmium myristate *[10196-67-5]*, $Cd(C_{14}H_{28}O_2)_2$, are of this type. Liquid stabilizers such as cadmium octoate *[2191-10-8]*, $Cd(C_8H_{15}O_2)_2$, cadmium phenolate *[18991-05-4]*, $Cd(C_6H_5O)_2$, cadmium decanoate *[2847-16-7]*, $Cd(C_{10}H_{20}O_2)_2$, cadmium benzoate *[3026-22-0]*, $Cd(C_7H_5O_2)_2$, and cadmium naphthenate are more versatile and economical in use and are prepared from CdO and the organic acid in an inert solvent. The water by-product is driven off as the reaction proceeds and the clear solution of cadmium soap in the organic solvent is used directly in plastics manufacture. FDA regulations have decreed that plastics that contact foodstuffs may not contain Cd–Ba stabilizers. Overall environmental concerns have led most plastics manufacturers to move away from heavy metal-based stabilizers, toward alternatives such as Ca–Zn materials (46). There has therefore been a decrease in consumption of Cd compounds in the stabilizer field that began in the late 1970s.

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CAFFEINE.

See ALKALOIDS.

CALCIUM AND CALCIUM ALLOYS

Calcium *[7440-70-2]*, Ca, a member of Group 2 (IIA) of the Periodic Table between magnesium and strontium, is classified, together with barium and strontium, as an alkaline-earth metal and is the lightest of the three. Calcium metal does not occur free in nature; however, in the form of numerous compounds, it is the fifth most abundant element constituting 3.63% of the earth's crust.

The word calcium is derived from calx, the Latin word for lime. The Romans used large quantities of calcium oxide or lime as mortar in construction (see LIME AND LIMESTONE). Because calcium compounds are very stable, elemental calcium was not produced until 1808 when a mercury amalgam resulted from electrolysis of calcium chloride in the presence of a mercury cathode. However, attempts to isolate the pure metal by distilling the mercury were only marginally successful.

Calcium metal was produced in 1855 by electrolysis of a mixture of calcium, strontium, and ammonium chlorides, but the product was highly contaminated with chlorides (1). By 1904 fairly large quantities of calcium were obtained by the electrolysis of molten calcium chloride held at a temperature above the melting point of the salt but below the melting point of calcium metal. An iron cathode just touched the surface of the bath and was raised slowly as the relatively chloride-free calcium solidified on the end. This process became the basis for commercial production of calcium metal until World War II.

Prior to 1939 calcium was manufactured exclusively in France and Germany. However, with the outbreak of World War II, an electrolytic calcium plant was constructed in the United States at Sault Ste. Marie, Michigan, by the Electro Metallurgical Corp. Large amounts of calcium were required as the reducing agent for uranium production (see URANIUM AND URANIUM COMPOUNDS). In addition, calcium was used to produce calcium hydride, which could easily be transported to remote areas and used as a source of hydrogen for meteorological balloons.

Calcium is mainly used as a reducing agent for many reactive, less common metals; to remove bismuth from lead (qv); as a desulfurizer and deoxidizer for ferrous metals and alloys; and as an alloying agent for aluminum, silicon, and lead. Small amounts are used as a dehydrating agent for organic solvents and as a purifying agent for removal of nitrogen and other impurities from argon and other rare gases (see HELIUM GROUP GASES).

Physical Properties

Pure calcium is a bright silvery white metal, although under normal atmospheric conditions freshly exposed surfaces of calcium quickly become covered with an oxide layer. The metal is extremely soft and ductile having a hardness between that of sodium and aluminum. It can be work-hardened to some degree by mechanical processing. Although its density is low, calcium's usefulness as a structural material is limited by low tensile strength and high chemical reactivity (2).

Calcium has a face-centered cubic crystal structure (a 0.5582 nm) at room temperature but transforms into a body-centered cubic (a 0.4477 nm) form at 428 ± 2°C (3). Some of the more important physical properties of calcium are given in Table 1. For additional physical properties, see references 7–12. Measurements of the physical properties of calcium are usually somewhat uncertain owing to the effects that small levels of impurities can exert.

Table 1. Physical Properties of Calcium[a]

Property	Value			
atomic weight	40.08			
electron configuration	$1s^2 2s^2 2p\ 3s^2 3p\ 4s^2$			
stable isotopes				
atomic weight 40 42 43	44		46	48
natural abundance, % 96.947 0.646 0.135	2.083		0.186	0.18
specific gravity at 20°C, kg m^3	1.55×10^3			
melting point, °C	839 ± 2			
boiling point, °C	1484			
heat of fusion, ΔH_{fus}, kJ mol[b]	9.2			
heat of vaporization, ΔH_{vap}, kJ mol[b]	161.5			
heat of combustion, kJ mol[b]	634.3			
vapor pressure				
pressure, kPa[c] 0.133 1.33	13.3		53.3	101.3
temperature, °C 800 970	1200		1390	1484
specific heat at 25°C, J (g·K)[b]	0.653			
coefficient of thermal expansion, 0–400°C, m (m·K)	22.3×10^{-6}			
electrical resistivity at 0°C, $\mu\Omega$·cm	3.91			
electron work function, eV	2.24			
tensile strength (annealed), MPa[c]	48			
yield strength (annealed), MPa[c]	13.7			
modulus of elasticity, GPa[c]	22.1–26.2			
hardness (as cast)				
HB[d]	16–18			
HR B[e]	36–40			

[a] Refs. 4–6.

[b] To convert J to cal, divide by 4.184.

[c] To convert kPa to psi, multiply by 0.145.

[d] Brinell Hardness scale.

[e] Rockwell B Hardness scale.

Chemical Properties

Calcium has a valence electron configuration of $4s^2$ and characteristically forms divalent compounds. It is very reactive and reacts vigorously with water, liberating hydrogen and forming calcium hydroxide, $Ca(OH)_2$. Calcium does not readily oxidize in dry air at room temperature but is quickly oxidized in moist air or in dry oxygen at about 300°C. The oxide layer is nonprotective and complete oxidation of a massive piece of calcium eventually occurs. Calcium reacts with fluorine at room temperature and with the other halogens at 400°C. When heated to 900°C, calcium reacts with nitrogen to form calcium nitride *[12013-82-0]*, Ca_3N_2 (see CALCIUM COMPOUNDS). The metal becomes incandescent when heated to 400–500°C in an atmosphere of hydrogen with the formation of calcium hydride *[7789-78-8]*, CaH_2, which reacts with water to give hydrogen:

$$CaH_2 + 2\,H_2O \rightarrow Ca(OH)_2 + 2\,H_2$$

Thus the hydride is a very efficient carrier of hydrogen. Upon heating, calcium reacts with boron, sulfur, carbon, and phosphorus to form the corresponding binary compounds and with carbon dioxide to form calcium carbide *[75-20-7]*, CaC_2, and calcium oxide *[1305-78-8]*, CaO.

Calcium is an excellent reducing agent and is widely used for this purpose. At elevated temperatures it reacts with the oxides or halides of almost all metallic elements to form the corresponding metal. It also combines with many metals forming a wide range of alloys and intermetallic compounds. Among the phase systems that have been better characterized are those with Ag, Al, Au, Bi, Cd, Co, Cu, Hg, Li, Na, Ni, Pb, Sb, Si, Sn, Tl, Zn, and the other Group 2 (IIA) metals (13).

Commercially produced calcium metal is analyzed for metallic impurities by emission spectroscopy. Carbon content is determined by combustion, whereas nitrogen is measured by Kjeldahl determination.

Manufacture

Electrolysis. Although in Western countries the aluminothermic process has now completely replaced the electrolytic method, electrolysis is believed to be the method used for calcium production in the People's Republic of China and the Commonwealth of Independent States (CIS). This process likely involves the production of a calcium–copper alloy, which is then redistilled to give calcium metal.

Aluminothermal Method. Calcium metal is produced by high temperature vacuum reduction of calcium oxide in the aluminothermal process. This process, in which aluminum *[7429-90-5]* metal serves as the reducing agent, was commercialized in the 1940s. The reactions, which are thermodynamically unfavorable at temperatures below 2000°C, have been summarized as:

$$6\,CaO + 2\,Al \rightleftharpoons 3CaO{\cdot}Al_2O_3 + 3\,Ca(g)$$

$$33\,CaO + 14\,Al \rightleftharpoons 12CaO{\cdot}7Al_2O_3 + 21\,Ca(g)$$

$$4\,CaO + 2\,Al \rightleftharpoons CaO{\cdot}Al_2O_3 + 3\,Ca(g)$$

In the range of 1000–1200°C a small but finite equilibrium pressure of calcium vapor is established. The calcium vapor is then transferred using a vacuum pump to a cooled region of the reactor where condensation takes place, shifting the equilibrium at the reaction site and allowing more calcium vapor to be formed.

A typical flow sheet for the process is given in Figure 1. High calcium limestone, $CaCO_3$, is quarried and calcined to form calcium oxide. The calcium oxide is ground to a small particle size and dry-blended with the desired amount of finely divided aluminum. This mixture is then compacted into briquettes to ensure good contact of reactants. The briquettes are placed in horizontal metal tubes, ie, retorts made of heat-resistant steel and heated in a furnace to 1100–1200°C. The open ends of the retorts protrude from the furnace and are cooled by water jackets to condense the calcium vapor. The retorts are then sealed and evacuated to a pressure of less than 13 Pa (0.1 mm Hg). After the reaction has been allowed to proceed for about 24 h the vacuum is broken with argon and the condensed blocks of ca 99% pure calcium metal, known as crowns, and calcium aluminate *[12042-78-3]* residue are removed. Large amounts of energy are required by this method, partially because of the high temperatures of the process and partially because of the energy-intensive raw materials employed, ie, the calcined CaO and electrolytically produced aluminum.

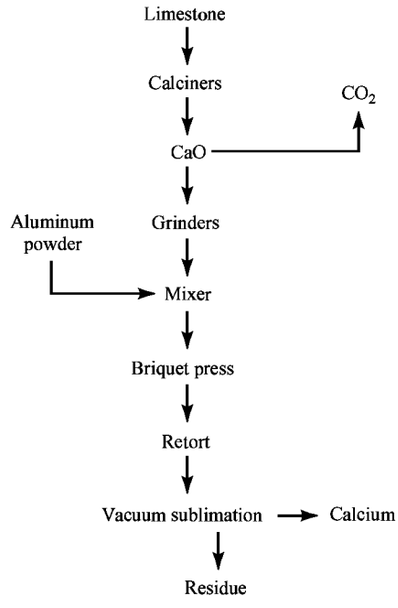

Fig. 1. Flow sheet for aluminum reduction process.

The calcium crowns can be sold as such for certain applications. However, further processing may be required, and the crowns can be reduced in size to pieces of about 25 cm or nodules of about 3 mm. They can also be melted under a protective atmosphere of argon and cast into billets or ingots. Calcium wire can be made by extrusion, and calcium turnings are produced as lathe cuttings from cast billets. Technologies have also been developed to manufacture calcium metal particulates and powders by atomization, comminution, and grinding processes.

Redistillation. For certain applications, especially those involving reduction of other metal compounds, better than 99% purity is required. This can be achieved by redistillation. In one method, crude calcium is placed in the bottom of a large vertical retort made of heat-resistant steel equipped with a water-cooled condenser at the top. The retort is sealed and evacuated to a pressure of less than 6.6 Pa (0.05 mm Hg) while the bottom is heated to 900–925°C. Under these conditions calcium quickly distills to the condensing section leaving behind the bulk of the less volatile impurities. Variations of this method have been used for commercial production. Subsequent processing must take place under exclusion of moisture to avoid oxidation.

Redistillation does not greatly reduce the impurity level of volatile materials such as magnesium. Volatile alkali metals can be separated from calcium by passing the vapors over refractory oxides such as TiO_2, ZrO_2, or Cr_2O_3 to form the nonvolatile Na_2O and K_2O (14). Purification techniques include reactive distillation (15), growth of crystals from the melt (16), and combined crystal growth and distillation techniques (17).

Shipment

Because of its extreme chemical reactivity, calcium metal must be carefully packaged for shipment and storage. The metal is packaged in sealed argon-filled containers. Calcium is classed as a flammable solid and is nonmailable. Sealed quantities of calcium should be stored in a dry, well-ventilated area so as to remove any hydrogen formed by reaction with moisture.

Specifications and Standards

The purity of commercial-grade calcium depends to a large extent on the purity of the calcium oxide used in its production. Impurities such as magnesium oxide, or other alkaline-earth or alkali metal compounds are reduced along with the calcium oxide, and these metals can contaminate the calcium. In addition, small amounts of aluminum may distill with the calcium vapor, and small amounts of calcium nitride may be produced by reaction with atmospheric nitrogen.

Redistilled-grade calcium still contains magnesium, which codistills with the calcium. For most applications the magnesium content is not detrimental. However, a grade known as center cut, consisting of the central portions of redistilled crowns, very low in magnesium, is also available. Magnesium tends to concentrate in the first metal fraction condensed; less volatile impurities tend to concentrate in the last fraction. Typical compositions of commercial- and redistilled-grade calcium are given in Table 2. Because of the high costs associated with the production of redistilled material, most of this highest purity calcium is imported from China.

Table 2. Compositional Analysis of Calcium Grades

	Composition, wt %	
Component	Commercial	Redistilled
Ca and Mg	99.5	99.9
Mg	0.70	0.70
Al	0.14	<0.0014
N	0.04	<0.0070
Fe	<0.034	<0.0017
Mn	<0.0088	<0.0016
Co		<0.0002
Li		<0.0001
Be		<0.0001
Cr		<0.0002
B		<0.0001

Economic Aspects

Calcium metal is produced in the United States by Pfizer Inc., Canaan, Connecticut, and in Canada by Timminco Metals, Toronto, Ontario. In France it is produced by Pechiney Electrometallurgie. It is also produced in the Commonwealth of Independent States (CIS) and the People's Republic of China. Both Pfizer and Timminco supply the various grades in a variety of sizes and forms. In addition, Pfizer supplies an 80% Ca–20% Mg alloy and a steel-clad calcium wire for use in deoxidation of steel and other metals. Timminco and Pfizer both supply ca 75% Ca–25% Al alloy for use in lead alloying. Timminco also supplies a 70% Mg–30% Ca alloy for use in lead debismuthizing (18), and calcium particulate products, which are purchased by several companies for the manufacture of cored wire for use in the steel industry.

U.S. imports of calcium metals fluctuate greatly. Since the mid-1980s, the availability of very low priced calcium metal from China and the CIS has led to substantial reductions in calcium production by Western producers. This has been compensated to a certain extent by an increase in sales of processed materials, ie, alloys and particulates, by the Western companies. In 1991, more than 700 tons of calcium metal were imported to the United States from the People's Republic of China. Significant quantities of calcium alloys and particulates have also been imported from France and Canada.

Although in the past calcium crown has been priced up to $8.95 kg, in the 1990s calcium has been priced as low as $5.00 kg by traders selling non-Western supply. Depending on the amount of processing involved, alloys and particulates may fetch prices in the range of $7–15 kg for large quantities.

Annual worldwide production is probably on the order of 2500 metric tons. Total worldwide production capacity is likely to be about 5000 metric tons.

In steelmaking applications, calcium disilicide has hitherto been generally more widely used than calcium metal. Total consumption of calcium disilicide in the steel industry worldwide is estimated to be about 6000 tons (30% Ca). Principal producers are Pechiney Electrometallurgie of France and SKW Trostberg of Germany. In the United States, the Norwegian company Elkem Metal produces up to 2500 metric tons of calcium disilicide. Also produced are CalSiBar, a calcium–silicon–barium alloy, and Hypercal, a calcium–silicon–barium–aluminum ferroalloy.

Health and Safety

Calcium metal and most calcium compounds are nontoxic. In massive pieces the metal does not spontaneously burn in air. Calcium can be touched with dry bare hands without harm. Care must be taken, however, to avoid contact with water owing to the exothermic liberation of hydrogen and the resulting explosion hazard. Calcium must always be kept dry and preferably sealed in the shipping containers.

Calcium Alloys

Calcium alloys can be produced by various techniques. However, direct alloying of the pure metals is normally used in the production of 80% calcium–magnesium, 70% magnesium–calcium, and 75% calcium–aluminum alloys.

Lead alloys containing small amounts of calcium are formed by plunging a basket containing a 77 or 75% calcium–23–25% Al alloy into a molten lead bath or by stirring the Ca–Al alloy into a vortex created by a mixing impellor (19).

Alloys of calcium with silicon are used in ferrous metallurgy (qv) and are generally produced in an electric furnace from CaO (or CaC_2), SiO_2, and a carbonaceous reducing agent (20). The resulting alloy, calcium disilicide *[12013-56-8]*, is nominally of composition $CaSi_2$ and has a typical wt % analysis of 30–33% Ca, 60–65% Si, 1.5–3% Fe (21). Proprietary Ca–Si alloys containing other elements such as Ba, Al, Ti, or Mn are sometimes produced by a combination of carbothermic ore reduction followed by direct alloying. In general, the chemical reactivity of calcium is greatly reduced when it is present in an alloyed state.

Uses

Calcium metal is an excellent reducing agent for production of the less common metals because of the large free energy of formation of its oxides and halides. The following metals have been prepared by the reduction of their oxides or fluorides with calcium: hafnium (22), plutonium (23), scandium (24), thorium (25), tungsten (26), uranium (27,28), vanadium (29), yttrium (30), zirconium (22,31), and most of the rare-earth metals (32).

For some processes, calcium metal first reacts with hydrogen to form calcium hydride, which is then used as the actual reducing agent. Oxides of uranium, vanadium, titanium, and niobium have been reduced in this way. Recently this technique has been used to reduce samarium oxide in the presence of cobalt powder to directly form the intermetallic compound samarium pentacobalt, $SmCo_5$, a material that is finding increased use in the manufacture of extremely powerful permanent magnets (33) (see MAGNETIC MATERIALS). Calciothermic reduction of neodymium fluoride (34) or neodymium oxide (35,36) has also been used for production of Nd metal or Nd–Fe alloys, which form the basis for the new family of Nd–Fe–B supermagnets (37,38). Additional amounts of calcium metal are converted into calcium hydride for use as a portable source of hydrogen gas (see HYDRIDES).

Calcium metal is also used in strip form as the anode material in thermal batteries (see BATTERIES), which are used as the power source in artillery fuses (39).

Metallurgical industries use large amounts of calcium and calcium-containing alloys for a variety of purposes. In ferrous metallurgy, calcium and certain of its alloys are used extensively as addition agents to deoxidize, desulfurize, and degas steel and cast iron; to control the type and distribution of nonmetallic inclusions in steel and to promote a uniform microstructure in gray iron (40–42). Because of its extreme reactivity, addition of pure calcium to molten steel can be difficult. Using alloys such as calcium–silicon may overcome this problem but introduces unwanted alloying elements into the iron (qv) or steel (qv). A newer promising technique to inject a steel-clad calcium wire into molten steel was developed in the 1970s (43). Application of this technology expanded greatly in the 1980s (44–46). Cored wires containing pure Ca may be diluted with Fe or CaSi to reduce the volatility of the reaction in molten steel. Alternatively, Ca-containing powders have been injected into molten steel via a refractory lance submerged in the ladle, with either nitrogen or argon as a carrier gas. Briquettes made of calcium and iron powders have also been used.

Calcium is used in the lead industry as a refining agent and as an alloying ingredient. When added to molten lead during refining, calcium and magnesium metals, or a 70% Mg–30% Ca alloy, form the basis of the Kroll-Betterton (KB) process, in which bismuth impurities are removed through the formation of the insoluble intermetallic compound Mg_2CaBi_2 (18,47,48). Bismuth levels can be reduced to less than 0.005% by this method. As an alloying ingredient, calcium is used at levels of 0.04–0.15% to increase the strength, creep resistance, corrosion resistance, and formability of lead (qv) (49). Because of their corrosion resistance to sulfuric acid (50), calcium-containing alloys are increasingly being used as grids in lead–acid storage batteries and have enabled development of the sealed maintenance-free auto battery (51,52) (see BATTERIES, SECONDARY, LEAD ACID).

The mechanical and electrical properties of aluminum alloys are improved through additions of small amounts of calcium (53). Such calcium-containing alloys are used for die casting of automobile trim. The eutectic alloy Al–Al_4Ca (7.6 wt % Ca) has been found to exhibit superplastic behavior (54). Other metallurgical uses of calcium include deoxidation of copper, magnesium, and tantalum (55). In the case of magnesium-base alloys, calcium also improves corrosion resistance and acts as a grain refiner.

A number of relatively minor uses for calcium depend on its high chemical reactivity. These include the dehydration of certain organic solvents, the desulfurization of petroleum, and the removal of nitrogen in the purification of argon gas. In addition, a number of calcium alloys have been patented for a variety of uses but apparently never commercialized. Among these are Ca–Li–Na and Ca–Li–Ba alloys for use as water-reactive solid fuels (56,57), a Ca–Li alloy for catalysis of the polymerization of conjugated diolefins (58), a Ca–Ag alloy for catalyzing the oxidation of ethylene to ethylene oxide (qv) (59), and Ca–Ge alloys for use as rectifier materials (60). Calcium–silicon alloys have been proposed for removing heavy metals from wastewaters and brine solutions (61).

An estimate of world calcium consumption in 1986 indicated that lead refining uses 30%; alloys, eg, with Pb, Al, and Si, 25%; steel treatment, 20%; calciothermic reduction, 10%; calcium hydride, 10%; and miscellaneous usage is 5%. More recent evidence, however, has suggested that increasing consumption of calcium in battery manufacture has made this the most significant use.

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Stephen G. Hibbins
Timminco Metals

CALCIUM CHANNEL ANTAGONISTS.

See CARDIOVASCULAR AGENTS.

CALCIUM COMPOUNDS

Survey,
Calcium carbonate,
Calcium chloride,
Calcium sulfate,

SURVEY

The chemical element calcium *[7440-70-2]*, Ca, atomic number 20, is an alkaline-earth metal which is fifth in abundance among all elements (ca 4%) and the third most abundant metal found in the earth's crust (1). It is too reactive to be found naturally in the free state, but its compounds are widespread as the minerals listed in Table 1 indicate. Calcite *[13397-26-7]*, $CaCO_3$, found as limestone, marble, and chalk, makes up approximately 7% of the earth's crust. Gypsum *[13397-24-5]*, $CaSO_4 \cdot 2H_2O$, fluorspar or fluorite *[7789-75-5]*, CaF_2, and dolomite *[16389-88-1]*, $CaCO_3 \cdot MgCO_3$, are other minerals that occur in sufficient quantities to serve as sources for elemental calcium. Lime feldspar *[1302-54-1]* (anorthite), $CaAl_2Si_2O_8$, accounts for more than half of the feldspars, which in turn make up some 60% of igneous rocks, eg, basalt and granite (2).

Table 1. Calcium-Containing Minerals

Mineral	CAS Registry Number	Molecular formula
marble		$CaCO_3$
limestone		$CaCO_3$
calcite	*[13397-26-7]*	$CaCO_3$
dolomite	*[17069-72-6]*	$CaCO_3 \cdot MgCO_3$
gypsum	*[13397-24-5]*	$CaSO_4 \cdot 2H_2O$
anhydrite	*[14798-04-0]*	$CaSO_4$
fluorspar	*[7789-75-5]*	CaF_2
fluorapatite	*[1306-05-4]*	$Ca_5F(PO_4)_3$
hydroxylapatite	*[1306-06-5]*	$Ca_5OH(PO_4)_3$
selenite	*[15698-85-8]*	$CaSO_4 \cdot 2H_2O$
anorthite	*[1302-54-1]*	$CaAl_2Si_2O_8$

The oceans contain vast quantities of ionic calcium, Ca^{2+}, to the extent of 400 mg L of seawater (3). Calcium is present in living organisms as a constituent of bones, teeth, shell, and coral. It is essential to plant as well as animal life.

Limestone and marble have been mined as building materials and the oxide of calcium, lime *[1305-78-8]*, has been used in the manufacture of mortar for centuries (see BUILDING MATERIALS, SURVEY; LIME AND LIMESTONE). Lime-burning was one of the first industries in the American colonies, where calcining of limestone was accomplished in kilns dug out of the sides of hills.

As befits the electron configuration of elemental calcium, the metal is very reactive, readily losing two valence electrons to form the dispositive ion. In aqueous solution and in its compounds, Ca^{2+} is colorless. Most calcium compounds are white, unless the cation is paired with a colored anion. The ion has only a weak tendency toward covalent bond formation.

Calcium reacts readily with water, oxygen, sulfur, and the halogens to form the respective ionic compounds calcium hydroxide *[1305-62-0]*, $Ca(OH)_2$, calcium oxide *[1305-78-8]*, CaO, calcium sulfide *[20548-54-3]*, CaS, and the calcium halides, CaX_2, where X F *[7789-75-5]*, Cl *[10035-04-8]*, Br *[7774-34-7]*, or I *[10102-68-8]*. This reactivity of the metal prevents it from being kept in air for any appreciable length of time. At elevated temperatures, calcium also combines directly with nitrogen, hydrogen, and carbon to form calcium nitride *[12013-82-0]*, Ca_3N_2, calcium hydride *[7789-78-8]*, CaH_2, and calcium carbide *[75-20-7]*, CaC_2, respectively.

Inorganic Compounds

Calcium Carbonate. Limestone is the most widely used of all rocks, as such for dimension stone or aggregate in concrete and road building, or as an industrial chemical and precursor of lime and hydrated lime. Calcium carbonate acts as a base in its application as a soil conditioner (agricultural lime is actually limestone), neutralizer of surface waters, industrial acid neutralizer, and in a limestone slurry as a stack gas scrubber to remove SO_2 (see SULFUR REMOVAL AND RECOVERY). Fluidized-bed combustion of coal using an admixture of pulverized limestone can be used to trap SO_2 before it reaches the exhaust stacks (see COAL CONVERSION PROCESSES). Precipitated calcium carbonate *[471-34-1]*, formed from carbonating suspensions of calcium hydroxide, is finding application as a mineral filler to give brightness and opacity to acid-free paper (4). Limestone is also used as a metallurgical flux.

Lime and Hydrated Lime. Lime, CaO, production in the United States in 1990 amounted to 15,820 metric tons ranking it fifth in tonnage of manufactured chemicals (5). More than 90% of the lime consumed in the United States is used for basic or industrial chemistry. It is produced by thermal decomposition (calcination) of calcium carbonate in various forms including limestone, marble, chalk, oyster shells, and dolomite. Although some purposes require 100% CaO lime, quicklimes used industrially almost always contain impurities such as MgO, SiO_2, Fe_2O_3, Al_2O_3, H_2O, and CO_2 (6). Quicklime containing less than 5% MgO is classified as high calcium lime, that which contains between 5 and 35% MgO, usually between 5 and 10%, is classified as magnesian lime, and lime containing more than 35% MgO, typically between 35 and 40%, is classified as dolomitic lime. Lime is strongly alkaline and has a negative temperature coefficient of solubility.

The hydrolysis process, ie, reaction with water, for lime is called slaking and produces hydrated lime, $Ca(OH)_2$. Calcium hydroxide is a strong base but has limited aqueous solubility, 0.219 g $Ca(OH)_2$ 100 g H_2O, and is therefore often used as a suspension. As an alkali it finds widespread industrial application because it is cheaper than sodium hydroxide.

Mortar. Mortar, principally slaked lime and sand, sets because of the evaporation of water, the deposition of calcium hydroxide, and the absorption of water by the bricks or cement blocks, followed by hardening as a result of the absorption and reaction of carbon dioxide.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

Metallurgy. Calcium oxide reacts readily with acid anhydrides:

$$CaO + SO_3 \rightarrow CaSO_4$$

Reactions of this type are important in high temperature metallurgical processes in which CaO, which may be produced by decomposition of $CaCO_3$, reacts with and removes acidic impurities, eg, in the pig-iron blast furnace (6).

$$CaO(\text{from limestone}) + SiO_2 \rightarrow CaSiO_3(\text{blast furnace slag})$$

In modern steel (qv) manufacture, pebble quicklime is used as a flux in the basic oxygen, basic open-hearth, basic Bessemer, and basic electric furnaces.

Treatment of Industrial Wastes. The alkaline nature and inexpensive price of lime make it ideal for treatment of acid waste liquors (6), including waste pickle liquids from steel plants, wastes from metal plating operations, eg, chrome and copper plating, acid wastes from chemical and explosives plants, and acid mine wastewaters.

Great quantities of stack gases containing acidic substances such as H_2S and SO_2 are produced in the smelting and refining of nonferrous metals such as copper, zinc, and lead obtained from sulfide ores. These can be trapped by stack gas scrubbers as a fine spray of lime, or limestone slurry in water is passed down the stack while the hot acidic gases are passing upwards. Control of emission of acid gases, primarily sulfur dioxide, from fossil fuel power plants is also accomplished with $Ca(OH)_2$ scrubbers (see AIR POLLUTION CONTROL METHODS). By-product calcium sulfite *[10257-55-3]*, $CaSO_3$, from this process must be dewatered (see DEWATERING) and eventually disposed of on land.

Cement (qv) and lime-based technologies are used to immobilize fly ash, cement kiln dust, ground blast furnace slag, and the sludges of sulfides, hydroxides, and phosphates of heavy metals, but not organic wastes that inhibit the setting process. Treatment of the concrete clinker with a sealant may be beneficial when acid leaching is a potential problem (7). Quicklime may be useful in chemically treating polychlorinated biphenyls (PCBs). The success of lime treatment of PCBs has been questioned, however (8).

Treatment of Municipal and Industrial Water Supplies. Hard water (qv) contains dissolved solids, chiefly calcium and magnesium salts. Water hardness results in the formation of insoluble curd from soap, decreased efficiency of detergents, and in the formation of mineral deposits that coat the surfaces of hot water systems, thereby clogging pipes and reducing heating efficiency. Feedwater softening treatment is necessary for boiler water and for water used in dyeing and other textile processing operations. On a large scale, the lime water-softening process is used to remove calcium and magnesium ions from water:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2\,CaCO_3(s) + 2\,H_2O$$

$$MgX_2 + Ca(OH)_2 \rightarrow Mg(OH)_2(s) + CaX_2$$

where X = Cl^-, NO_3^-, HCO_3^-, $\frac{1}{2}SO_4^{2-}$, $\frac{1}{2}CO_3^{2-}$. The composition of the raw hard water must be monitored so that an excess of slaked lime is not added.

Other Applications. Among other industrial uses of lime are: causticizing agent in kraft (sulfate) paper (qv) plants; recovery of ammonia (qv) from NH_4Cl (Solvay process); recovery of magnesium (qv) from seawater and brines via precipitation of $Mg(OH)_2$; production of pesticides such as calcium arsenate, lime–sulfur sprays, and Bordeaux mixture, which is copper sulfate and lime in water; and neutralizing acid soils (6,9,10). Lime is used in the manufacture of several products: in pigments (qv), where satin white is calcium aluminate-hydrated calcium sulfate; in protective and bonding agents for water paints (qv) to serve as rust inhibitor, fire resistance, waterproofing agent, and disinfectant; in glues, such as calcium caseinate; and in gelatin. It is used in refining of beet and cane sugar (qv) and in the treatment of corn prior to conversion to corn meal for tortillas.

Halogen Compounds.

Halides. Calcium halides are made by reaction of elemental calcium and the halogens directly or more conveniently by the reaction of the corresponding hydrohalic acid and $CaCO_3$, CaO, or $Ca(OH)_2$.

Fluorspar *[7789-75-5]*, CaF_2, is used as a flux in metallurgical processes such as production of steel in the open-hearth furnace. Pure crystals of this salt have applications in spectroscopy where transparency to visible and ultraviolet radiation is a requirement. CaF_2 is also the precursor for HF (see FLUORINE COMPOUNDS, INORGANIC) and fluorine (qv). $CaCl_2$ in its anhydrous form finds application as an industrial and laboratory drying agent because of its deliquescent properties. Water–$CaCl_2$ solutions are used as refrigeration fluids.

Hypochlorites. A common dry form of chlorine used as a bleach or water purifier is made by reaction of gaseous chlorine and high calcium hydrated lime:

$$Ca(OH)_2 + Cl_2 \rightarrow CaCl(OCl)\cdot H_2O$$

This product, called chloride of lime *[67560-00-3]* or bleaching powder, has about 35% available chlorine.

Another bleaching agent, calcium hypochlorite *[7778-54-3]*, $Ca(OCl)_2$, available chlorine ca 70%, can be made by salting out from a solution of bleaching powder with NaCl. In contrast with bleaching powder, calcium hypochlorite does not decompose on standing (see BLEACHING AGENTS).

Sulfates and Sulfites. Calcium sulfate *[7778-18-9]* occurs in large deposits as $CaSO_4$ and as gypsum, $CaSO_4\cdot 2H_2O$. The dihydrate is a functional additive in Portland cement to control setting time. Gypsum loses some of its water of hydration on heating to near 100°C and forms plaster of Paris, the hemihydrate, approximately as shown:

$$2\,CaSO_4\cdot 2\,H_2O \rightarrow 2\,CaSO_4\frac{1}{2}H_2O + 3\,H_2O$$

The reaction reverses when water is added to plaster of Paris and the mixture sets back to the dihydrate accompanied by a slight increase in volume and the evolution of heat.

Calcium sulfite *[10257-55-3]* and acid sulfite may be prepared by reaction of SO_2 and hydrated lime or limestone. Calcium acid sulfite *[13780-03-5]*, $Ca(HSO_3)_2$, has been used to remove lignin (qv) from wood pulp in paper manufacture (6) (see PAPER; PULP).

Phosphates. The primary constituent of phosphate rock is fluorapatite, $Ca_5FP_3O_{12}$. Industrial phosphates including phosphate fertilizers (qv), phosphoric acid, and calcium phosphates (11) (see PHOSPHORIC ACID AND THE PHOSPHATES) are obtained from the large deposits of fluorapatite found in Florida in the United States, and in Morocco. Because phosphate rock is too insoluble to be useful as a fertilizer, it is converted to superphosphate *[12431-88-8]*, $Ca(H_2PO_4)_2 + 2\,CaSO_4$, by H_2SO_4 and to triple superphosphate *[7758-23-8]*, $Ca(H_2PO_4)_2$, by H_3PO_4 (12). Phosphoric acid may also be produced from phosphate rock by reaction with H_2SO_4.

Calcium metaphosphate *[13477-39-9]* is made by reaction of P_2O_5 in HPO_3 with rock phosphate. The insoluble, polymeric product must be hydrolyzed before it can act as a fertilizer (13):

$$[Ca(PO_3)_2]_x + 2xH_2O \rightarrow xCa(H_2PO_4)_2$$

Monocalcium phosphate *[10031-30-8]*, $Ca(H_2PO_4)_2\cdot H_2O$, used in baking powder (see BAKERY PROCESSES AND LEAVENING AGENTS), is crystallized from a hot reaction mixture of concentrated (electric furnace) phosphoric acid and lime, or it is made by spray-drying a slurry of the product of reaction of lime and phosphoric acid (14).

Calcium Magnesium Acetate. Calcium magnesium acetate *[76123-46-1]* (CMA), suggested formula $CaMg_2(C_2H_3O_2)$ (15), is an emerging bulk chemical that has found application as a replacement for salt and calcium chloride as a less corrosive and biodegradable road deicer. CMA has been used as a precursor for calcination processes and to capture sulfur during the combustion of lower grade coals.

Hydride. Calcium hydride *[7789-78-8]*, CaH_2, is an effective reducing agent at high temperatures and has been used to reduce inorganic oxides to their metals. The hydride, which evolves hydrogen smoothly on reaction with water, has found application as a convenient solid source for hydrogen gas. The compound is a convenient drying agent for gases and organic solvents.

Silicates.

Glass. Ordinary glass (qv), soda–lime glass, is a complex mixture of silicates, chiefly those of sodium and calcium *[1344-95-2]* (6,9). Lime, usually

dolomitic lime, follows sand, soda ash, and limestone as the fourth most important raw material in the manufacture of glass. The selection of lime versus limestone as starting material is frequently decided by the design of the manufacturing plant.

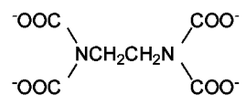
Portland Cement. Portland cement is obtained by calcining a mixture of substances to produce an appropriate ratio of the oxides CaO, MgO, Al_2O_3, Fe_2O_3, and SiO_2 (9) (see CEMENT).

Whitewares (Earthenware, China, Porcelain). The chief raw materials of ceramic manufacture are clay, feldspar, and sand (9). All of the three common types of feldspars are used: soda, potash, $M_2O{\cdot}Al_2O_3{\cdot}6SiO_2$, M Na, K, and lime (see CERAMICS; ENAMELS). Clays (qv), hydrated aluminum silicates such as kaolinite *[1318-74-7]*, $Al_2(Si_2O_7)\cdot 2H_2O$, are formed by the weathering of igneous rocks such as feldspars (6). Fluxing agents include the calcium compounds apatite, fluorspar, and calcined bones (mainly apatite). Special refractory ingredients may be lime, limestone, or dolomite.

Calcium Silicate Brick. Sand–lime brick is used in masonry in the same way as common clay brick. The bricks, molded from a wet mixture of sand and high calcium hydrated lime, are heated under pressure in a steam atmosphere. Complex hydrosilicates are formed that give the bricks high dimensional stability (6).

Coordination Chemistry of Calcium

Calcium ion shows some tendency to form complexes mainly through coordination with oxygen-containing ligands. An important example is citrate which chelates Ca^{2+} in water solution and can reduce the effective calcium ion concentration in blood below the level that results in triggering the coagulation process (see BLOOD, COAGULANTS AND ANTICOAGULANTS). Ethylenediaminetetraacetate (EDTA, Versene, Sequestrene)



has an extremely large formation constant for its 1:1 complex with Ca^{2+} (11) (see CHELATING AGENTS). EDTA is also used as an anticoagulant for stored blood and as a reagent in volumetric analysis for calcium ion.

Ca^{2+} can be complexed by crown ethers and cryptate ligands and in this form can be transported across natural and artificial membranes.

A few calcium complexes having nitrogen ligands are known. Calcium halides form addition complexes with NH_3 such as $CaCl_2 nNH_3$ (n 2,4,8) and $CaBr_2 nNH_3$ (n 2,4,6,8). Hexaammine calcium *[12133-31-2]*, $Ca(NH_3)$, is formed by reaction of calcium metal and anhydrous NH_3 (11) (see COORDINATION COMPOUNDS).

Organic Chemistry of Calcium

Calcium Carbide and its Derivatives. Although hydrocarbon-based acetylene production has become more important, early manufacture of acetylene was based on manufacture of the intermediate, calcium carbide *[75-20-7]*, CaC_2. This ionic acetylide is produced by reaction of lime and carbon in electric-arc furnaces (16).

$$CaO + 3C \rightarrow CaC_2 + CO$$

Calcium carbide can be treated with water to produce acetylene from which other organic compounds, eg, ethanol, acetaldehyde, may be obtained (6) (see ACETYLENE DERIVED CHEMICALS; CARBIDES).

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2 \text{(acetylene)}$$

Calcium carbide is also used to produce calcium cyanamide *[156-62-7]*, $CaCN_2$, (see CYANAMIDES).

$$CaC_2 + N_2 \rightarrow CaCN_2 + C$$

Calcium cyanamide (lime nitrogen) has been used as a fertilizer (6). It hydrolyzes in moist soil to produce ammonia:

$$CaCN_2 + 3H_2O \rightarrow CaCO_3 + 2NH_3$$

Calcium cyanamide can be converted to calcium cyanide [592-01-8], used in cyanidation of metallic ores and production of sodium cyanide and ferrocyanides (11) (see CYANIDES). Calcium cyanamide has also been used to make cyanamide which in turn is the starting material for important industrial organic syntheses.

Salts of Organic Acids. Calcium salts of organic acids may be prepared by reaction of the carbonate hydroxide and the organic acid (9). Calcium lactate *[814-80-2]* is an intermediate in the purification of lactic acid from fermentation of molasses. Calcium soaps, soaps of fatty acids, are soluble in hydrocarbons, and are useful as waterproofing agents and constituents of greases (9).

In production of sugar, the juice extracted from the sugar cane or sugar beets is treated with a suspension of $Ca(OH)_2$, which neutralizes the syrup acidity and precipitates calcium sucrate, leaving impurities in the solution. This is filtered and the calcium sucrate is converted to sugar and $CaCO_3$ by reaction with CO_2.

Reagents in Synthesis. Calcium borohydride *[17068-95-0]*, $Ca(BH_4)_2$, produced by reaction of $NaBH_4$ and $CaCl_2$, has been used for reductions (see HYDRIDES). Hexaamminecalcium *[12133-31-2]*, prepared by passing NH_3 into an ether suspension of calcium, reduces polycyclic aromatic compounds leaving one isolated aromatic ring. Calcium hydride, CaH_2, and anhydrous calcium sulfate (Drierite), $CaSO_4$, are useful as drying agents (17).

Organometallic Chemistry. Only a few organocalcium compounds have been reported. Alkyl calcium halides have been prepared by reaction of the halides and calcium in tetrahydrofuran (17).

Biological Role of Calcium

Biological functions of Ca(II) ion are numerous but may be classified in one of three categories: the formation of solid skeletal material such as bone, teeth, and shell; the stabilizing of protein conformational structure; and the most varied, the ability of Ca(II) to trigger certain physiological activities such as muscle contraction and the release of hormones (qv).

The insoluble Ca(II) salts of weak acids, such as calcium phosphate, carbonate, and oxalate, serve as the hard structural material in bone, dentine, enamel, shells, etc. About 99% of the calcium found in the human body appears in mineral form in the bones and teeth. Calcium accounts for approximately 2% of body weight (18,19). The mineral in bones and teeth is mostly hydroxyapatite *[1306-06-5]* having unit cell composition $Ca_{10}(PO_4)(OH)_2$. The mineralization process in bone follows prior protein matrix formation. A calcium pumping mechanism raises the concentrations of Ca(II) and phosphate within bone cells to the level of supersaturation. Granules of amorphous calcium phosphate precipitate and are released to the outside of the bone cell. There the amorphous calcium phosphate, which may make up as much as 30–40% of the mineral in adult bone, is recrystallized to crystallites of hydroxyapatite preferentially at bone collagen sites. These small crystallites do not exceed 10 nm in diameter (20).

The Ca(II) concentration in blood is closely controlled: normal values lie between 2.1 and 2.6 mmol L (8.5–10.4 mg dL) of serum (21). The free calcium ion concentration is near 1.2 mmol L; the rest is chelated with blood proteins or, to a lesser extent, with citrate. It is the free Ca(II) in the serum that determines the calcium balance with the tissues. The mineral phase of bone is essentially in chemical equilibrium with calcium and phosphate ions present in blood serum, and bone cells can easily promote either the deposition or dissolution of the mineral phase by localized changes in pH or chelating

compounds. Treatment for osteoporosis, the loss of bone mineral that occurs in the aged, especially in postmenopausal women, commonly includes dietary calcium supplements. Excessive calcium ingestion can lead to a problem for those prone to stone formation in the urinary tract.

Three hormones regulate turnover of calcium in the body (22). 1,25-Dihydroxycholecalciferol is a steroid derivative made by the combined action of the skin, liver, and kidneys, or furnished by dietary factors with vitamin D activity. The apparent action of this compound is to promote the transcription of genes for proteins that facilitate transport of calcium and phosphate ions through the plasma membrane. Parathormone (PTH) is a polypeptide hormone secreted by the parathyroid gland, in response to a fall in extracellular Ca(II). It acts on bones and kidneys in concert with 1,25-dihydroxycholecalciferol to stimulate resorption of bone and reabsorption of calcium from the glomerular filtrate. Calcitonin, the third hormone, is a polypeptide secreted by the thyroid gland in response to a rise in blood Ca(II) concentration. Its production leads to an increase in bone deposition, increased loss of calcium and phosphate in the urine, and inhibition of the synthesis of 1,25-dihydroxycholecalciferol.

Calcium is essential to several steps in the enzyme cascade of the blood clotting process, such as the conversion of prothrombin to thrombin (23). Clotting can be inhibited in stored blood supplies by addition of complexing agents such as EDTA or citrate which reduce the levels of the free ion, Ca(II).

Calcium is the trigger behind the muscle contraction process (24,25). Neural stimulation activates the release of stored Ca(II) resulting in a dramatic increase in free calcium ion levels. The subsequent binding of Ca(II) resulting in a dramatic increase in free calcium ion levels. The subsequent binding of Ca(II) to the muscle protein troponin C provides the impetus for a conformational change in the troponin complex and sets off successive events resulting in muscle contraction.

The influx of Ca(II) across the presynaptic membrane is essential for nerve signal transmission involving excitation by acetylcholine (26). Calcium is important in transducing regulatory signals across many membranes and is an important secondary messenger hormone. The increase in intracellular Ca(II) levels can result from either active transport of Ca(II) across the membrane via an import channel or by release of Ca(II) from reticulum stores within the cell. More than 30 different proteins have been linked to regulation by the calcium complex with calmodulin (27,28).

The recommended daily allowances of calcium are: children to 10 years of age, 360–800 mg; teenage children, 1200 mg; adults, 800 mg, increasing to 1200 mg during pregnancy and lactation (29). Cow's milk supplies ca 1.27 g L of calcium in available form.

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CALCIUM CARBONATE

Calcium carbonate *[471-34-1]*, $CaCO_3$, mol wt 100.09, occurs naturally as the principal constituent of limestone, marble, and chalk. Powdered calcium carbonate is produced by two methods on the industrial scale. It is quarried and ground from naturally occurring deposits and in some cases beneficiated. It is also made by precipitation from dissolved calcium hydroxide and carbon dioxide. The natural ground calcium carbonate and the precipitated material compete industrially based primarily on particle size and the characteristics imparted to a product.

Natural ground calcium carbonate has been used for years as the primary constituent of putty. Since 1945, the processing of natural calcium carbonate has seen the introduction of beneficiation by flotation (qv) to remove impurities and the development of grinding processes to manufacture finer products. Precipitated calcium carbonate was first introduced in England in 1850; commercial production started in the United States in about 1913.

Calcium carbonate is one of the most versatile mineral fillers (qv) and is consumed in a wide range of products including paper (qv), paint (qv), plastics, rubber, textiles (qv), caulks, sealants (qv), and printing inks (qv). High purity grades of both natural and precipitated calcium carbonate meet the requirements of the *Food Chemicals Codex* and the *United States Pharmacopeia* and are used in dentifrices (qv), cosmetics (qv), foods, and pharmaceuticals (qv).

Properties

Calcium carbonate occurs naturally in three crystal structures: calcite *[13397-26-7]*, aragonite *[14791-73-2]*, and, although rarely, vaterite. Calcite is thermodynamically stable, aragonite is metastable and irreversibly changes to calcite when heated in dry air to about 400°C. Vaterite is metastable to calcite and aragonite under geological conditions but is found during the high temperature precipitation of calcium carbonate (1). The crystal forms of calcite are in the hexagonal system with $\bar{3}2$ m symmetry; the crystals are varied in habit and over 300 different forms have been described. Aragonite is orthorhombic with 2 m2 m2 m symmetry and three crystal habits are common: acicular pyramidal, tabular, and pseudohexagonal (2).

The commercial grades of calcium carbonate from natural sources are either calcite, aragonite, or sedimentary chalk. In most precipitated grades aragonite is the predominant crystal structure. The essential properties of the two common crystal structures are shown in Table 1.

Table 1. Properties of Calcium Carbonate

Property[a]	Calcite	Aragonite
specific gravity	2.60–2.75	2.92–2.94
hardness, Mohs'	3.0	3.5–4.0
solubility at 18°C, g 100 g H_2O	0.0013	0.0019
melting point, °C	1339[b]	[c]
	dec 900	
index of refraction[d]		
α		1.530
β		1.680
γ		1.685
ω	1.658	
ε	1.486	

[a] Ref. 3.

[b] At 10.38 MPa (102.5 atm).

[c] Decomposes to calcite at temperatures >400°C.

[d] Ref. 2.

Manufacturing and Processing

Natural Calcium Carbonate. The production of natural ground calcium carbonate starts with the quarrying of a deposit of chalk, limestone, or marble. The best deposits for most industrial applications are those having a high (>90% $CaCO_3$) purity and high brightness. Most calcium carbonate quarries are of the open-pit type but there are underground operations. The ore is taken to a primary crusher for size reduction and then into the processing plant. The plant process is dependent on the grade of material being made. Typically, coarse products that do not require high purity, 90–98% $CaCO_3$, go to secondary crushing. This may be a cone- or jaw-type crusher that produces material minus 4 cm. Final grinding for products down to approximately 5 μm median particle size can be done in a roller mill or ball mill. Products finer than 10 μm often involve additional processing, usually in a dry ball mill circuit with air classification.

For those grades requiring high purity or finer material the process is different. Ideally, the secondary crushing step should reduce the ore to the point where mineral impurities are liberated, typically <100 μm, without producing an excess of fines. The material may then be beneficiated through a mineral flotation process in which impurities are floated out. The flotation process produces a higher brightness material that is typically >98% calcium carbonate. Commonly, the flotation product is further ground in a ball mill to produce a product in the 2–50 μm particle range. Products having a median particle size less than 2 μm are usually wet ground in media or sand mills, the final product being a slurry that can be shipped after stabilizers and biocides are added, or dried for powdered products.

Precipitated Calcium Carbonate. Precipitated calcium carbonate can be produced by several methods but only the carbonation process is commercially used in the United States. Limestone is calcined in a kiln to obtain carbon dioxide and quicklime. The quicklime is mixed with water to produce a milk-of-lime. Dry hydrated lime can also be used as a feedstock. Carbon dioxide gas is bubbled through the milk-of-lime in a reactor known as a carbonator. Gassing continues until the calcium hydroxide has been converted to the carbonate. The end point can be monitored chemically or by pH measurements. Reaction conditions determine the type of crystal, the size of particles, and the size distribution produced.

The reactions in this method are

$$\text{calcination } CaCO_3 \rightarrow CaO + CO_2$$

$$\text{hydration or slaking } CaO + H_2O \rightarrow Ca(OH)_2$$

$$\text{carbonation } Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

Following carbonation, the product can be further purified by screening. This screening, also used to control the maximum size of the product, is followed by dewatering (qv). Rotary vacuum filters, pressure filters, or centrifuges are used in the mechanical removal of water. Final drying is accomplished as with natural calcium carbonate in either a rotary, spray, or flash dryer. Products having mean particle sizes from submicrometers (~0.03 μm) to several micrometers are available.

Both natural ground or precipitated calcium carbonate are available as dry products shipped in 22.7 kg multiwall bags, supersacks, or in bulk via truck and railcar. Calcium carbonate slurry, primarily used by the paper industry, is shipped by truck and rail. The solids content of these slurries is typically >70% by weight for ground products and 20–50% for precipitated. In the 1980s small precipitation plants were built at the site of large North American papermills.

Some grades of calcium carbonate are surface coated to improve handling properties and dispersability in plastics. Treatments used are fatty acids, resins, and wetting agents. Coating reduces the surface energy, thereby facilitating dispersion in organic binders.

Economic Aspects

The calcium carbonate industry is one of the most competitive of the industrial minerals industry. The market for fine products (97% <45 μm) is estimated to be between 5–9 million tons annually in the United States. The pricing is dependent on the grade which is determined by fineness, purity, and brightness; it ranges from 3¢ kg for coarse materials to over 44¢ kg for some ultrafine coated or food grades (4).

The primary U.S. producers of ground calcium carbonate are Columbia River Carbonates, ECC International, Franklin Limestone Co., Genstar Stone Products, Georgia Marble Company, J.M. Huber Corp., Calcium Carbonates Division, James River Limestone Co., Inc., OMYA Inc. (Pluess-Staufer), and Pfizer Inc. The principal U.S. producers of precipitated products are Mississippi Lime Co. and Pfizer Inc.

Specifications, Standards, and Quality Control

The most comprehensive set of test methods for calcium carbonate has been assembled by the Pulverized Limestone Division of the National Stone Association. Methods for particle size, brightness, +325 mesh (44 μm), and percentage of calcium carbonate have been published; standards are available and have been well characterized (5). The Technical Association of the Pulp and Paper Industry (TAPPI) has published methods for calcium carbonate used in the paper industry (6).

Food and pharmaceutical grades of calcium carbonate are covered by the *Food Chemicals Codex* (7) and the *United States Pharmacopeia* (8) and subject to U.S. Food and Drug Administration Good Manufacturing Practices (9). Both purity requirements and test methods are available (7,8). Calcium carbonate is listed in the *U.S. Code of Federal Regulation* as a food additive, and is authorized for use in both paper and plastic food contact applications.

Health and Safety Factors

Calcium carbonate is listed as a food additive (7) and not considered a toxic material. The exposure to dust is regulated and a Threshold Limit Value–Time-Weighted Average (TLV–TWA) of 10 mg m^3 is set (10). Both natural ground and precipitated calcium carbonates can contain low levels of impurities that are regulated. The impurities depend on the source of material, processing, and the final grade; impurities are typically trace metals and naturally occurring minerals.

Uses

The use of calcium carbonate in paint, paper, and plastics make up the principal part of the market. In the paper industry calcium carbonate products find two uses: as a filler in the papermaking process and as a part of the coating on paper.

The demand for calcium carbonate in papermaking has been driven by the change to alkaline from acid papermaking. This change, motivated by demands for higher brightness, greater permanency in paper, and economics, started in Europe in the 1960s and began to take hold in North America in the 1980s. Approximately half of the mills in North America producing printing and writing papers use the alkaline process and 90% are projected to do so by the year 2000 (4). The benefits of calcium carbonate are brighter paper, greater resistance to yellowing and aging, and the economic advantage of substituting inexpensive calcium carbonate for expensive pulp (qv). Depending on paper grade and applications, calcium carbonate can be 25% or more of the sheet. Both ground natural and precipitated calcium carbonate are used as paper fillers depending on the application. Blends of ground and precipitated calcium carbonate have found use in an effort to optimize the properties of both products (see PAPERMAKING ADDITIVES) (11).

The other significant market for calcium carbonate in paper is as the pigment in paper coatings. Paper is coated to improve its brightness, opacity, printability, ink receptivity, and smoothness. Ultra fine (<1 μm mean particle size) ground calcium carbonate, in addition to providing these properties, improves the rheology of coating formulations applied at coater speeds up to 1600 m min. Calcium carbonate may be the sole pigment in the formulation or may be used in combination with other fillers (qv) such as kaolin (see CLAYS). In coating applications the use of ground natural calcium carbonate far exceeds that of precipitated material.

The plastics industry is a primary consumer of calcium carbonate products. Flexible and rigid PVC, polyolefins, thermosets, and elastomers (qv), including rubber, utilize a wide variety of coated and uncoated grades. Each of these plastics categories benefit by calcium carbonate's lower cost in relation to the polymer. In addition to cost savings, the use of calcium carbonate provides improvements in modulus, heat resistance, hardness, shrinkage reduction, and color fastness. Increases in impact strength and improvements in stability are also benefits, especially with the use of coated grades.

The use of calcium carbonate in thermosets continues to grow as these plastics replace alternative materials, especially in automotive applications. Increased loadings of calcium carbonate in thermosets reduce cost and provide better surface characteristics.

Calcium carbonate is one of the most common filler extenders used in the paint and coatings industry. Consumer and contractor paint formulas can include products from submicrometer size to coarse mesh sizes. The main function of calcium carbonate in paint is as a low cost extender. It is also used to improve brightness, application properties, stability, and exposure resistance. Coarse products help to lower gloss and sheen or even provide textured finishes. The selection of product type and particle size is determined by the desired performance and cost of the coating.

Calcium carbonate is also used in industrial finishes and powder coatings. These paints typically include finer products; the primary purpose is rheological and gloss control. Calcium carbonate is also used in paints to extend and enhance the use of titanium dioxide. This is accomplished by using the finest of natural ground products or precipitated grades.

Calcium carbonate continues to be used in its original application, putty, as well as caulks, sealants (qv), adhesives (qv), and printing inks (qv). Large volumes are used in carpet backing and in joint cements. It is used to improve body, reinforcement, and other properties.

Calcium carbonate is finding increasing use in flue gas desulfurization. This application by a variety of engineering processes traps the sulfur–oxygen compounds produced in the combustion of coal (qv) (see COAL CONVERSION PROCESS; EXHAUST CONTROL, INDUSTRIAL; SULFUR REMOVAL AND RECOVERY).

Calcium carbonate is used in food and pharmaceutical applications for both its chemical and physical properties. It is used as an antacid, as a calcium supplement in foods, as a mild abrasive in toothpaste, and in chewing gum to name only a few (see FOOD ADDITIVES).

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CALCIUM CHLORIDE

Calcium chloride *[10043-52-4]*, $CaCl_2$, is a white, crystalline salt that is very soluble in water. Solutions containing 30–45 wt % $CaCl_2$ are used commercially. Of the alkaline-earth chlorides it is the most soluble in water. It is extremely hygroscopic and liberates large amounts of heat during water absorption and on dissolution. It forms a series of hydrates containing one, two, four, and six moles of water per mole of calcium chloride (Table 1). Another hydrate, $CaCl_2 \cdot 0.33H_2O$, has been identified, mol wt 116.98; 94.8 wt % $CaCl_2$; heat of solution in water to infinite dilution, 71.37 kJ/mol (17.06 kcal/mol) (1,2).

Table 1. Properties of Calcium Chloride Hydrates

Property	$CaCl_2 \cdot 6H_2O$	$CaCl_2 \cdot 4H_2O$	$CaCl_2 \cdot 2H_2O$	$CaCl_2 \cdot H_2O$	$CaCl_2$
CAS Registry Number	*[7774-34-7]*	*[25094-02-4]*	*[10035-04-8]*	*[22691-02-7]*	*[10043-52-4]*
mol wt	219.09	183.05	147.02	129.00	110.99
composition, wt % $CaCl_2$	50.66	60.63	75.49	86.03	100.00
mp, °C	30.08	45.13	176	187	772
sp gravity, d_4^{25}	1.71	1.83	1.85	2.24	2.16
heat of fusion or transition, kJ/mol[a]	43.4[b]	30.6[b]	12.9	17.3	28.5
heat of solution in water[c], kJ/mol[a]	15.8	10.8	44.05[d]	52.16[d]	81.85[d]
heat of formation, at 25°C, kJ/mol[a]	2608	2010	1403	1109	795.4
heat capacity, at 25°C, J/(g·°C)[a]	1.66[b]	1.35[b]	1.17[b]	0.84	0.67

[a] To convert J to cal, divide by 4.184.

[b] Ref. 1.

[c] To infinite dilution.

[d] Ref. 2.

Commercial applications of calcium chloride and its hydrates exploit one or more of its properties with regard to aqueous solubility, hygroscopic nature, the heat gained or lost when one hydrated phase changes to another, and the depressed freezing point of the eutectic solution at a composition of about 30% by weight calcium chloride.

Properties

The properties of calcium chloride and its hydrates are summarized in Table 1. Accurate data are now available for the heats of fusion of the hexahydrate, the incongruent fusion of the tetrahydrate, and the molar heat capacities of the hexahydrate, tetrahydrate, and dihydrate (1). These data are important when considering the calcium chloride hydrates as thermal storage media. A reevaluation and extension of the phase relationships of the calcium chloride hydrates, has led to new values for the heats of infinite dilution for the dihydrate, monohydrate, 0.33-hydrate, and pure calcium chloride (1).

A study on the solubility of calcium chloride hydrates (3) has generated polymonials relating the weight percent of anhydrous salt in a saturated solution to temperature (°C). For $9.33 < t°C < 28.16$

$$\text{wt\%}CaCl_2 = 1.783 + 28.93\,t^{0.5} - 7.70\,t + 0.73\,t^{1.5}$$

for $33.54 < t°C < 44.81$

$$\text{wt\%}CaCl_2 = 238.3 + 146.6\,t^{0.5} - 25.47\,t + 1.51\,t^{1.5}$$

for $49.37 < t°C < 97.65$

$$\text{wt\%}CaCl_2 = 39.17 + 5.28\,t^{0.5} - 0.624\,t + 0.03\,t^{1.5}$$

These three equations represent saturation with respect to the hexahydrate, tetrahydrate, and dihydrate in the temperature ranges indicated. The phase relationships among calcium chloride, its hydrates, and a saturated solution are illustrated in the diagram in Figure 1.

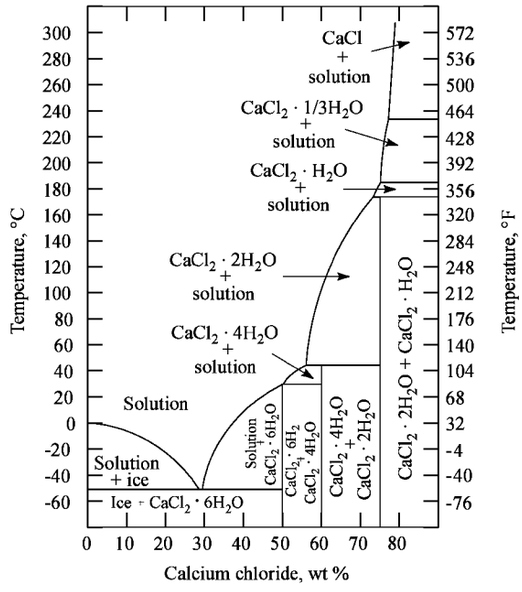

Fig. 1. The phase relationships among calcium chloride, its hydrates, and a saturated solution.

Calcium Chloride Solutions. Because of high solubility in water, calcium chloride is used to obtain solutions having relatively high densities. For example, densities as high as 1430 kg/m^3 are achieved at 20°C and as high as 1570 kg/m^3 at 80°C. The oil and gas drilling industries frequently exploit these high densities when completing or reworking wells. Density, or specific gravity, can also be used to determine the molal concentration, c, of calcium chloride in water (4).

$$c = 30.8 - 129.6\,d + 180.8\,d^2 - 106.8\,d^3 + 24.89\,d^4$$

where c is in units of moles of calcium chloride per kg of water and d is the specific gravity of solution relative to water at 25°C. The densities of calcium chloride solution at various wt % $CaCl_2$ values and different temperatures have been listed (5). Densities and apparent molar volumes of aqueous calcium chloride solutions at temperatures from 323 K (50°C) to 600 K (327°C) and at pressures up to 40 MPa (395 atm) have also been reported (6).

Viscosity is an important property of calcium chloride solutions in terms of engineering design and in application of such solutions to flow through porous media. Data and equations for estimating viscosities of calcium chloride solutions over the temperature range of 20–50°C are available (4). For example, at 25°C and in the concentration range from 0.27 to 5.1 molal (2.87–36.1 wt %) $CaCl_2$, the viscosity increases from 0.96 to 5.10 mPa·s (cP).

Numerous studies on the thermodynamics of calcium chloride solutions were published in the 1980s. Many of these were oriented toward verifying and expanding the Pitzer equations for determination of activity coefficients and other parameters in electrolyte solutions of high ionic strength. A review article covering much of this work is available (7). Application of Pitzer equations to the modeling of brine density as a function of composition, temperature, and pressure has been successfully carried out (8).

Production and Consumption

Significant quantities of calcium chloride are produced in the United States, Canada, Mexico, Germany, Belgium, Sweden, Finland, Norway, and Japan. Historically calcium chloride was a by-product of sodium carbonate (soda ash) production. The sole U.S. producer via this route closed operation in the 1980s and consolidated production in Canada.

In the United States the primary route for making calcium chloride is by the evaporation of underground brines (see CHEMICALS FROM BRINES). Additional commercial material is available by the action of hydrochloric acid on limestone. Typically the hydrochloric acid is a by-product of some other commercial process and the conversion to calcium chloride is motivated by waste avoidance (see HYDROGEN CHLORIDE).

There are 10 producers of calcium chloride solutions in the United States, three of these also make a dry product. Solution production is centered around Michigan (brines), California and Utah (brines), and Louisiana (by-product acid). The majority of dry calcium chloride is made in Michigan, lesser quantities in Louisiana, and minor quantities in California. Production involves removal of other chlorides (primarily magnesium) by precipitation and filtration followed by concentration of the calcium chloride solution, either for ultimate sale, or for feed for dry product. Commercial dry products vary by the amount of water removed and by the nature of the drying equipment used. Production and capacity figures for the United States are indicated in Table 2.

Table 2. Calcium Chloride Production and Capacity

Date	$CaCl_2$, wt %	Quantity, t/yr	Quantity corrected to 100 wt % $CaCl_2$, t/yr	Reference
1988	75	596,000[a]	447,200[a]	9
1989[b]	100	726,700[c]	726,700[c]	10
1990[b]	77	1,011,000[c]	778,200[c]	11

[a] Production estimate.

[b] Data given in middle of the year.

[c] Capacity estimate.

Apparent $CaCl_2$ consumption (12,13) ranged from a low of 572,400 to a high of 688,600 metric tons from 1984 to 1988. This is a smaller variation than in the estimated production figures which were 704,900 metric tons, 100 wt % basis for 1984 (10).

Estimated imports of calcium chloride increased more than tenfold between 1984 and 1988, from 10,000 to 139,700 metric tons on a 100 wt % basis (10). Import figures (12) do not distinguish between solution or dry calcium chloride or the purity of dry products. Thus estimates of imported quantities involve an assessment of the mix of products imported and ultimate conversion to 100% basis. Imports in 1989 totaled 119,000 metric tons, 75% of which were from Canada (12). Canada is the principal trading partner with the United States for calcium chloride because of use as a deicing chemical and the

location of production facilities close to the border in both countries. Other significant foreign sources in 1989 were Mexico, 17,800 metric tons; West Germany, 6,900 metric tons; and Sweden, 4,800 metric tons. Historical trends are summarized (9,10).

Exports for 1989 totaled 20,100 metric tons, 71% to Canada (13). Exports consist of mixed dry products having 77%, 90%, and 94–97% purity. Export figures underestimate the volume of calcium chloride traded because some calcium chloride is exported under use designations.

Specifications and Pricing

Most solution calcium chloride is sold as 38 wt % or 45 wt % concentration, however different uses require concentrations ranging from 28 wt % to 45 wt %. Producers ship the most concentrated form and final adjustments in concentration are made by distributors.

The majority of dry calcium chloride comes in one of two forms: flake or pellet. Lesser amounts are sold as mini pellets, powders, or briquettes. Six agencies grade calcium chloride (Table 3). The American Society of Testing Materials (ASTM) specifications include calcium chloride content (assay), total alkali chlorides (<8.0% as NaCl), total magnesium (<0.5% as magnesium chloride), and other impurities (<1.0% after accounting for sodium, calcium, potassium, and magnesium chlorides, water and calcium hydroxide). These specifications are written for a product containing 90.5% calcium chloride, prorated adjustments are required for assays less than 90.5%. Calcium chloride manufactured in the United States routinely meets these standards. Table 4 summarizes sieve analyses for key commercial grades.

Table 3. Calcium Chloride Specifications

Specification	Uses	Products specified	Reference
ASTM D98–87, AASHTO[a] M144–86	road conditioning maintenance; curing concrete	solution: unspecified concentrations; dry: three grades based on 77%, 90%, and 94% minimum assay	14,15
AWWA[b] B550–90	treatment of municipal and industrial water supplies	dry: as flake, pellet, or granular powder or briquette	16
FCC third ed.	sequesterant in food, cross-linker, firming agent in canning, multipurpose food additive	solution: unspecified concentrations; dry: dihydrate 99–107% of formula weights; anhydrous: 93.0% $CaCl_2$ minimum	17
ACS reagent chemicals	reagent-grade	dihydrate: 74–78% $CaCl_2$	18
	desiccant-grade	not less than 96% $CaCl_2$	
USP XXII reagent specifications	dihydrate and anhydrous for drying	use ACS specifications for dihydrate and anhydrous	19
USP XXII	general	dihydrate: 99–107% $CaCl_2 \cdot 2\ H_2O$; calcium chloride for injections, sterile solution in water, 95–105% of labeled $CaCl_2 \cdot 2\ H_2O$	

[a] AASHTO = American Association of State Highway and Transportation Officials.

[b] AWWA = American Water Works Association.

Table 4. Sieve Analysis for $CaCl_2$ Commercial Grades, Mass %, Passing[a]

Class, solid form	Sieve size, mm[b]					
	31.5	9.5	4.75 (No. 4)	2.36 (No. 8)	0.830 (No. 20)	0.600 (No. 30)
			Grade 1, 77 wt % $CaCl_2$ min			
A, flake		100	80–100			0–5
B, granular		100	0–80			0–5
			Grade 2, 90 wt % $CaCl_2$ min			
A, flake		100	80–100			0–5
B, pellets		100	80–100		0–10	0–5
C, granular	100		0–5			
D, powder			100	80–100		0–65
			Grade 3, 94 wt % $CaCl_2$ min			
A, flake		100	80–100			0–5
B, pellets		100	80–100		0–10	0–5
C, granular	100		0–5			
D, powder			100	80–100		0–65

[a] ASTM specifications.

[b] Mesh number appears in parentheses.

Calcium chloride meeting *Food Chemicals Codex* (FCC), specifications is used as a direct and indirect food additive. Chemical specifications for anhydrous calcium chloride include: assay, not less than 93.0%; arsenic (as As), <3 ppm; fluoride, <0.004%; heavy metals (as Pb), <0.002%; lead, <10 ppm; magnesium and alkali salts, <5%; acid insoluble matter, <0.02%; and no particles of sample greater than 2 mm in any dimension. Each agency includes methods of sampling, testing, packaging, and shipping within the specifications. Additionally, The American Concrete Institute (ACI) specifies the uses of calcium chloride for its members (20–23).

Dry calcium chloride is sold in bulk for transporting via rail cars, hopper trucks, and sparger cars. It is also sold in mini bulk bags, drums, bags, and boxes. Liquid is offered in barges, tank cars, tank trucks, and drums. Not all producers offer all packaging alternatives. Rebaggers and distributors handle smaller package sizes, typically 45.5 kg drums to 2.3 kg bags. December 1990 prices were: for carloads of 77–80% $CaCl_2$ flake, \$181.88 t in bulk and \$236.99 t in 45.5 kg bags; for bulk or 36.3 kg bag carloads of 94–97% anhydrous pellets or flake, \$358.25 t; for tank car, truckload, or barge quantity of 30–42% solution, \$124.64 t of $CaCl_2$ on a 100% basis; and for a truckload of freight equalized 124.74 kg drums of USP granular $CaCl_2$, \$.36 kg. All prices, except for that of USP granular material, are ex-works (11). Historical trends in pricing are available (9,10).

Uses

Calcium chloride, manufactured for over 100 years, has been used for a variety of purposes. The primary $CaCl_2$ markets have not changed since the 1950s. Significant markets in the United States are for deicing during the winter and roadbed stabilization, and as a dust palliative during the summer. Use as an accelerator in the ready-mix concrete industry is sizeable but there is concern about chloride usage because of the possible corrosion of steel in highways and buildings. Calcium chloride is also used in oil and gas well drilling. The size of that market is dependent on the state of the worldwide oil and gas industry.

Deicing. All forms of calcium chloride are used in conjunction with other products to deice pavement, driveways, and sidewalks. Anhydrous, 94–97 wt % calcium chloride pellets and 77–80 wt % calcium chloride flakes are used for highway deicing and in institutional and consumer markets. Calcium chloride solutions of 28–32 wt % concentration are used for prewetting rock salt or abrasives such as sand or cinders before spreading on highways. Solutions of 42–45 wt % concentration are also used to pretreat stockpiles of these materials. Calcium chloride is the deicer of choice for use at temperatures < 6.7°C (24–26).

Roadbed Stabilization/Dust Control. One of the earliest uses of calcium chloride was for dust control and roadbed stabilization of unpaved gravel roads. Calcium chloride in both dry and solution forms are used both topically and mixed with the aggregate. When a calcium chloride solution is sprayed on a dusty road surface, it absorbs moisture from the atmosphere binding the dust particles and keeping the surface damp. Calcium chloride does not evaporate, thus this dust-free condition is retained over a long period of time.

If aggregate is mixed with dry calcium chloride or a calcium chloride solution and then compacted, the presence of the calcium chloride draws in moisture to bind the fine particles in the aggregate matrix. This process leads to a well compacted, maximum density gravel road. This application for calcium chloride was reviewed in 1958 (27). More recent publications are also available (28–30).

Accelerator in Ready-Mix Concrete. Calcium chloride accelerates the set time of concrete giving it a high early strength development. It is not an antifreeze, but by using it during cold weather protection can proceed in a timely manner (31–34). In Russia, calcium chloride forms a component of several antifreeze admixtures (33). Reviews of the concerns and possible remedies of calcium chloride corrosion problems in concrete are available (21,35). There is no consensus on what the safe levels of calcium chloride in concrete are.

Oilfield Uses. Calcium chloride has two uses in the oilfield: as a primary ingredient in completion fluids and as the brine phase in an invert emulsion oil mud. An excellent review of oil well drilling fluids is available (36) (see also PETROLEUM, DRILLING FLUIDS).

Food. Food-grade calcium chloride is used in cheese making to aid in rennet coagulation and to replace calcium lost in pasteurization. In the canning industry it is used to firm the skin of fruit such as tomatoes, cucumbers, and jalapenos. It acts as a control in many flocculation, coagulation systems (37). Food-grade calcium chloride is used in the brewing industry both to control the mineral salt characteristics of the water and as a basic component of certain beers (see BEER).

Other Uses. Calcium chloride has several other uses, some of which have been superseded by alternative products or processes in the United States, however the technology is still relevant in other countries. Miscellaneous uses of calcium chloride are in the adhesives (qv) industry as a humectant; in animal feed (see FEEDS AND FEED ADDITIVES) as a calcium source; in the manufacture of chemicals and plastics for precipitation of insoluble inorganics, as a suspending agent in suspension polymerization, as a catalyst, and for cation-exchange reactions with sodium; in ceramics (qv) for porosity reduction, and as a precursor for high purity ceramics; in dye manufacture (see DYES AND DYE INTERMEDIATES) as a precipitating agent; in energy storage for thermal storage; in food processing (qv) as a refrigerant; for fruits and vegetable processing and packaging as a refrigerant and desiccant; in gas processing as a desiccant (see DESICCANTS); as an antifreeze for highway impact attenuators; in lighting as an intermediate in manufacturing phosphors and in refining tungsten ores; in the production of metals and in mining for heavy media separation of coal and ores, tire ballasting, removal of nonferrous impurities in iron ore processing, and control of alkalies in blast furnaces; in petroleum refining as both a refrigerant and desiccant; in pulp (qv) and paper (qv) manufacture as a drainage aid, refrigerant, and desiccant; and in waste treatment for the precipitation of various inorganic salts and the emulsion breaking flotation of oily wastes.

Toxicity and Environmental

Calcium is a macronutrient essential for all organisms. Chlorine is a micronutrient essential for higher (ie, seed) plants but not considered essential for mammals. Above certain levels chloride is toxic to plants and animals, thus when considering calcium chloride, potentially large concentrations of calcium ion can be tolerated, but at these concentrations the chloride ion becomes toxic.

Calcium is readily abundant in the mammalian diet. A 70 kg human contains approximately 1200 g of calcium and has a daily intake of 1100 mg day. There are no published exposure limits (38). Low levels of calcium in the blood, hypocalcemia, can lead to tetany; high levels, hypercalcemia, can lead to coma and death. Calcium toxicity, above 160 mg L in the blood, is not related to an excessive intake of calcium.

Calcium chloride solutions, typically employed at 2–5% concentration, are used as antispasmodics, diuretics (qv), and in the treatment of tetany. Concentrated solutions of calcium chloride cause erythema, exfoliation, ulceration, and scarring of the skin (39). Injections into the tissue may cause necrosis. If given orally calcium chloride can cause irritation to the gastrointestinal tract unless accompanied by a demulcent. There is no published information on mutagenicity or carcinogenicity caused by calcium ions or calcium chloride. Calcium chloride has been given a toxicity or hazard level 3 (40). Materials in this classification typically have LD_{50} below 400 mg kg or an LC_{50} below 100 ppm.

Calcium chloride is found in the marine environment. The elemental composition of seawater is 400 ppm calcium, 18,900 ppm chlorine, and many organisms and aquatic species are tolerant of these concentrations. Toxicity arises either from the invasion of freshwater in otherwise saltwater environments or possible toxic doses of calcium chloride from spills, surface runoff, or underground percolation into typically freshwater streams or aquifers. Various agencies have guidelines for calcium and chloride in potable water (41). The European Economic Community (EEC) is the only agency to have a minimum specification for calcium in softened water.

Both calcium and chloride ions are essential to plant biota, although only small amounts of chloride ion are needed. The average concentration of calcium in plant shoot dry matter sufficient for adequate growth is 0.5%. The corresponding number for chloride is 100 mg kg (42).

The ability of plants to take up calcium chloride (ion selectivity) and the toxicity of calcium chloride in plants and soils varies widely (43–45). Studies of herbaceous crop species, where water deficit is not a constraint, point to low levels of chloride ion as responsible for inhibiting growth (46). Deicing salts can be toxic to roadside vegetation (47). The use of both calcium chloride and sodium chloride as deicing salts and the effects on various grasses, shrubs, and trees has been the focus of both experimental and field studies (48). Evidence points to chloride ion as the primary cause of toxic events. From studies in Europe, calcium chloride in blends of deicing salts can have beneficial effects on the regulation of sodium, and of potassium over sodium, in spruce trees (49). Recommendations for calcium chloride tolerant species are available (48,50).

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CALCIUM SULFATE

Calcium sulfate *[7778-18-9]*, $CaSO_4$, in mineral form is commonly called gypsum and occurs abundantly in many areas of the world. In natural deposits, the main form is the dihydrate. Some anhydrite is also present in most areas, although to a lesser extent. Mineral composition can be found in Table 1.

Table 1. Gypsum Forms and Composition

Common name	CAS Registry Number	Molecular formula	Composition, wt %		
			CaO	SO_3	Combined H_2O
anhydrite	*[7778-18-9]*	$CaSO_4$	41.2	58.8	
gypsum	*[10101-41-4]*	$CaSO_4 \cdot 2H_2O$	32.6	46.5	20.9
stucco	*[10034-76-1]*	$CaSO_4 \cdot \frac{1}{2} H_2O$	38.6	55.2	6.2

The hemihydrate (stucco) is normally produced by heat conversion of the dihydrate from which 3 2 H_2O is removed as vapor. The resulting powder is also known as plaster of Paris *[26499-65-0]*. Stucco has the greatest commercial significance of these materials. It is the primary constituent used to fabricate products and in formulated plasters used in job- or shop-site applications.

About 23 million metric tons of gypsum are consumed annually. About 80% is processed into the commercially usable hemihydrate. Uses of gypsum are in fabricated and or formulated building materials (see BUILDING MATERIALS, SURVEY), Portland cement (qv) set regulation, and agricultural soil conditioning.

Gypsum and its dehydrated form have been used by builders and artists in ornamental and structural applications for more than 5000 years as evidenced by artifacts from the ancient Egyptian and Greek cultures. Processing of gypsum to the hemihydrate in the United States began about 1835 using ore imported from the Canadian Maritime Provinces. Methods for control of the set (hydration time) of hemihydrate conversion to dihydrate were developed by the end of the nineteenth century. This factor, along with the desirable natural property of fire resistance, led to the growth of a significant industry that produces boards and plasters as the primary wall cladding materials in modern building construction.

Properties

Table 2 lists the physical properties of calcium sulfate.

Table 2. Physical Properties of Calcium Sulfate

Property	Dihydrate	Hemihydrate	Anhydrite
mol wt	172.17	145.15	136.14
transition point, °C	128[a] 163[b]	163[b]	
mp[c], °C	1450	1450	1450
specific gravity	2.32		2.96
solubility at 25°C, g 100 g H_2O	0.24	0.30	0.20
hardness, Mohs'	1.5–2.0		3.0–3.5

[a] Hemihydrate is formed.

[b] Anhydrous material is formed.

[c] Compound decomposes.

Sources

The natural, or mineral, form of gypsum is most widely extracted by mining or quarrying and used commercially. Natural gypsum is rarely found in a pure form. The dihydrate and anhydrous forms are commonly found together. Impurities in gypsum deposits typically include calcium and magnesium carbonates, oxide(s) of silicon, clays, and small amounts of various soluble salts. The last two items generally have the most undesirable effect on commercial processing and production of prefabricated products. In some cases, the crude ore is beneficiated to provide a commercial feedstock in which the percentage of functional dihydrate has been increased. Most gypsum commercially used has a purity level of 80% or higher.

The natural ore is quarried or mined in many areas of North America and Europe. Leading North American regions include Canada, Mexico, and in the United States, California, Texas, Nevada, Iowa, Kansas, Ohio, Indiana, and Michigan. In Europe, France, Spain, Italy, the United Kingdom, and Russia have significant deposits of natural gypsum, as does Germany.

Gypsum is found in a variety of natural mineral forms. Most notable is the massive, or rocklike form commonly used in commercial manufacturing operations. However, there are other unique forms of special interest. Among these are alabaster, a fine-grained, relatively soft, rather pure gypsum used almost exclusively by sculptors. Colorado is the principal commercial source in the United States, although alabaster is occasionally found in other deposits. Satin spar is also a pure form of crystalline gypsum that is fibrous in nature. It is translucent in its dense form. Another unique form of gypsum is selenite, high in purity and monoclinic in form. It frequently occurs as an intrusion in more rocklike deposits, but large sheets, up to several meters, of selenite have been found. Sometimes selenite is mistaken for mica because of its platey structure and transparency.

Anhydrite, the anhydrous form of calcium sulfate, occurs frequently in natural mineral deposits. It is naturally dense, and because of its massive state and typical dark grey color, it can usually be distinguished visually from the dihydrate. In addition to occurring naturally, $CaSO_4$ can be obtained by high temperature dehydration of gypsum dihydrate, or by precipitation, although these are not significant factors in the gypsum industry.

Gypsum is also obtained as a by-product of various chemical processes. The main sources are from processes involving scrubbing gases evolved in

burning fuels that contain sulfur (see SULFUR REMOVAL AND RECOVERY), such as coal (qv) used in electrical power generating plants (see also COAL CONVERSION PROCESSES), and the chemical synthesis of chemicals, such as sulfuric acid, phosphoric acid, titanium dioxide, citric acid, and organic polymers. In general, the added capital investment and processing costs associated with rendering by-product gypsums suitable as feedstocks for the gypsum board and plaster industry have tended to deter their use where good quality and relatively low cost natural gypsums are readily available. However, high gypsum purity makes by-product sources attractive, especially in regions where natural gypsum is scarce. A notable example of this has been Japan wherein large tonnages of by-product gypsum from its phosphoric acid industry have been used (see PHOSPHORIC ACID AND THE PHOSPHATES). In North America, little phosphogypsum has been used because of objectionable impurities and or properties. In all areas of the world where gypsum is used, more focus has been given to other sources, ie, chiefly from stack gas scrubbing processes or flue gas desulfurization (FGD).

Decomposition Thermodynamics

The thermodynamic properties of gypsum decomposition, which involve two distinct steps,

$$CaSO_4 \cdot 2H_2O \xrightarrow{\Delta} CaSO_4 \cdot \frac{1}{2}H_2O + 1\frac{1}{2}H_2O$$

$$CaSO_4 \cdot \frac{1}{2}H_2O \xrightarrow{\Delta} CaSO_4 + \frac{1}{2}H_2O$$

have been the subject of much theoretical and practical study. Two forms of the hemihydrate, α and β, have been identified (1). The β-form is obtained when the dihydrate is partly dehydrated in a vacuum at 100°C or under conditions lacking a nearly saturated steam atmosphere. The α-form is prepared by dehydration of gypsum in water at temperatures above 97°C and by dissociation in an atmosphere of saturated steam.

The terms α and β are often used to differentiate two generally accepted, yet controversial forms of hemihydrate. The β-hemihydrate has a higher energy content and a higher solubility than the α-hemihydrate. The α-form is distinguishable from the β-form in that α-form particles disintegrate very little when mixed with water and far less mixing water is required to form a workable slurry. Consequently, the α-form has the ability to produce denser and higher compressive-strength casts and less excess water has to be removed after hydration is complete.

Anhydrite also has several common classifications. Anhydrite I designates the natural rock form. Anhydrite II identifies a relatively insoluble form of $CaSO_4$ prepared by high temperature thermal decomposition of the dihydrate. It has an orthorhombic lattice. Anhydrite III, a relatively soluble form made by lower temperature decomposition of dihydrate, is quite unstable converting to hemihydrate easily upon exposure to water or free moisture, and has the same crystal lattice as the hemihydrate phase. Soluble anhydrite is readily made from gypsum by dehydration at temperatures of 140–200°C. Insoluble anhydrite can be made by heating the dihydrate, hemihydrate, or soluble anhydrite for about 1 h at 900°C. Conversion can also be achieved at lower temperatures; however, longer times are necessary.

Manufacture

Natural Gypsum. Gypsum rock from the mine or quarry is crushed and sized to meet the requirements of future processing or removed for direct marketing of the dihydrate as a cement retarder. Once subjected to a secondary crusher, calcining, and drying, the product is fine-ground. Fine-ground dihydrate is commonly called land plaster, regardless of its intended use. The degree of fine grinding is dictated by the ultimate use. The majority of fine-ground dihydrate is used as feed to calcination processes for conversion to hemihydrate.

β-Hemihydrate. The dehydration of gypsum, commonly referred to as calcination in the gypsum industry, is used to prepare hemihydrate, or anhydrite. Hemihydrate is generally called stucco in North America and plaster in many other continents. In North America, plaster is differentiated from hemihydrate or stucco by the inclusion of additives to control intended use properties, eg, rehydration time, density, coverage, strength, and viscosity.

Kettle calcination continues to be the most commonly used method of producing β-hemihydrate. The kettle can be operated on either a batch or continuous basis. Its construction is shown in Figure 1. The kettle is a cylindrical steel vessel enclosed in a refractory shell with a plenum between. The steel vessel is suspended above a fire box from which heated air flows up and into the plenum surrounding the steel vessel and through multiple horizontal flues that completely penetrate the vessel. The plenum and flues provide heat to the kettle contents before the heated air is exhausted. An agitator with horizontal arms penetrates the depth of the kettle and is driven from above. Land plaster, usually ground 85–95% through 100 mesh (149 μm) is fed from the top. In batch operation, using an 18.1 metric ton capacity kettle, filling takes 20–30 min. Another 90–120 min are usually required to convert the dihydrate to hemihydrate. The steam released from the dehydration reaction is vented from the kettle top. When conversion to hemihydrate is complete (usually determined by temperature measurement of the kettle contents), the stucco is discharged by gravity through the quick-opening gate located at the periphery and bottom of the steel vessel. A typical temperature pattern for the kettle contents is shown in Figure 2. Approximately 1 GJ/t (950,000 Btu/t) of hemihydrate is required in a well-designed kettle.

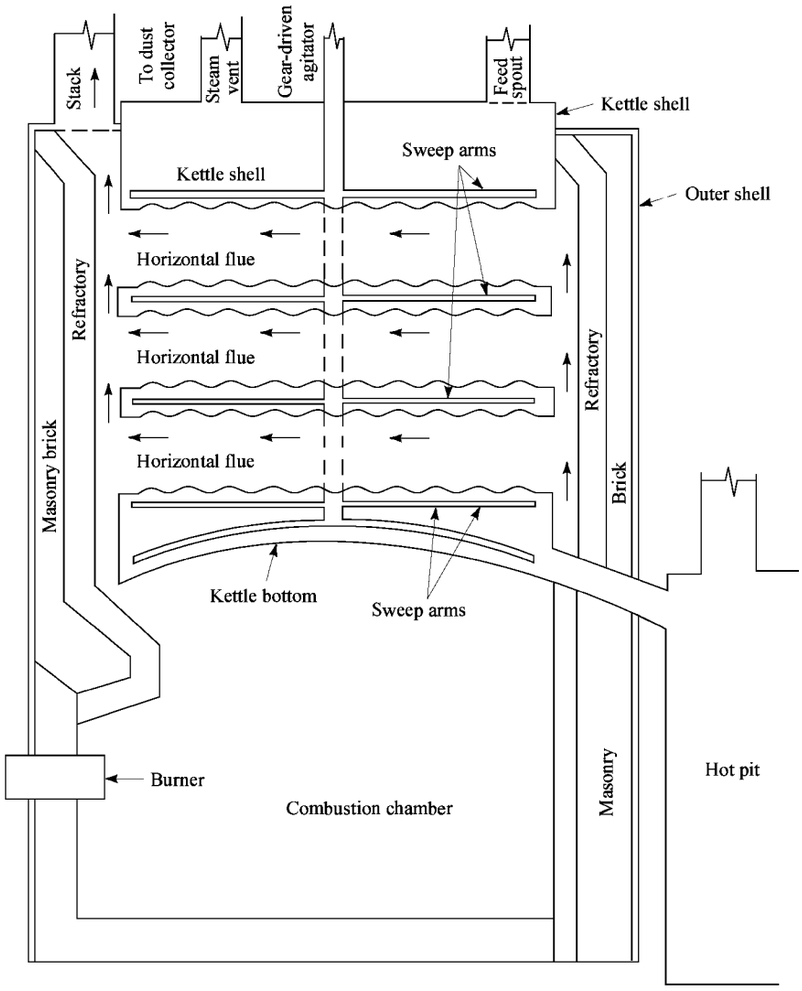

Fig. 1. Generalized vertical cross-section of a calcining kettle.

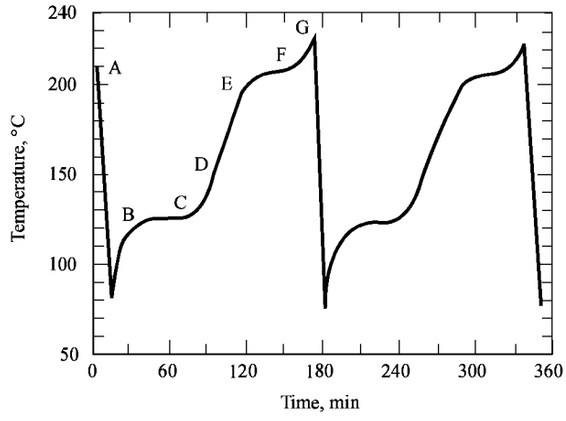

Fig. 2. Time–temperature profile for kettle calcination. Points A–B represent the fill period; B–C, the boil or drag; C–D, falling rate or cook-off; D, discharge for hemihydrate. Points D–E show firing rate to second boil; E–F, second boil; F–G, second cook-off; G, second-settle discharge.

During the fill portion of a kettle cycle, firing rate is usually controlled to maintain the kettle contents at a temperature of approximately 104°C. When the fill is complete, the firing rate is increased to a level dictated by the desired stucco properties. The mass boils at a temperature of 115–120°C. The boil or drag continues for about 1 h, then subsides. Heating continues for a short time period to allow moisture release and the mass temperature increases to approximately 150–155°C if the hemihydrate form is desired, after which firing is reduced and the contents dumped. In practice, owing to the inability to heat all particles of gypsum adequately, the discharged mass often contains small percentages of dihydrate, soluble anhydrite, and at times insoluble anhydrite.

If soluble anhydrite is desired, firing is maintained until a second boil occurs accompanied by a second temperature plateau at about 190°C. Virtually all the water of crystallization has been removed at 215°C. Soluble salts are impurities that increase the vapor pressure within the kettle. Aridized stucco refers to kettle-calcined hemihydrate that has been made with the intentional addition of 0.55–1.1 kilograms of NaCl or $CaCl_2$ per metric ton of land plaster. The stucco characteristic of lower water demand permits higher density and higher strength casts. The hygroscopic nature of the chlorides prevents the use of aridized stucco for some applications.

In another process water is introduced into the hot calcined gypsum mass in a kettle to reduce the temperature of a portion of the mass to below the boiling point of water. The mass is then reheated (2). Stabilized setting and water demand properties are claimed as are water demand levels below those attainable through aridizing.

There is also a technique that permits continuous calcination using kettles (3). A continuous perforated grate charged with a single layer or multiple layers of sized rock has been designed (4) where the bed passes through a machine wherein hot gases are drawn through the bed. The material is cooled by air at a selected point to control the degree of dehydration.

An air-suspension calcination process for the commercial production of hemihydrate (stucco) from dihydrate gypsum has been patented (5). A schematic representation of this continuous process is shown in Figure 3. Gypsum particles are in intimate contact with heated process air so that only a few seconds of residence time in the process chamber is required to effect dehydration. The β-type material produced is characterized by a high activity level having a naturally rapid time for rehydration to dihydrate, ie, setting time. This process is particularly favorable for commercial fabrication of board. These calcining units are in routine use throughout North America and, in the 1980s, use was extended to Europe and Australia.

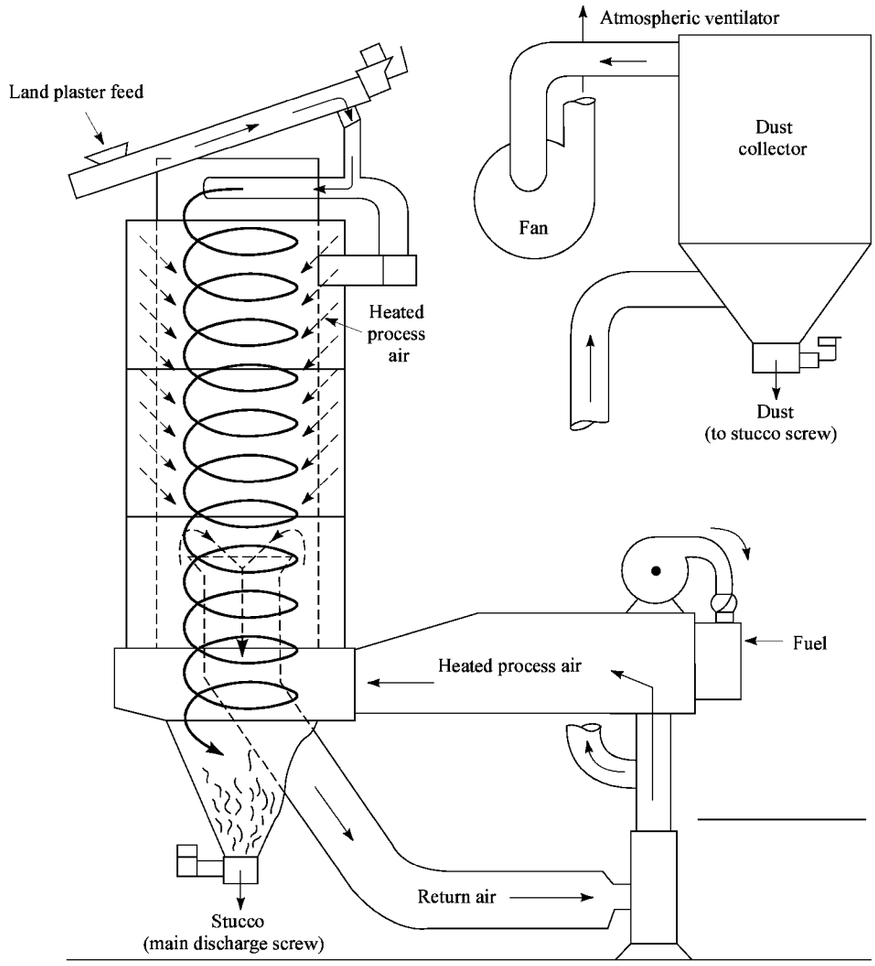

Fig. 3. Generalized vertical cross-section of a calcidyne calciner (5).

α-Hemihydrate. Three processing methods are used for the production of α-hemihydrate. One, developed in the 1930s, involves charging lump gypsum rock 1.3–5 cm in size into a vertical retort, sealing it, and applying steam at a pressure of 117 kPa (17 psi) and a temperature of about 123°C (6). After calcination under these conditions for 5–7 h the hot moist rock is quickly dried and pulverized.

Another method (7), first reported in the 1950s, has lower water demand. The dihydrate is heated in a water solution containing a metallic salt, such as $CaCl_2$, at pressures not exceeding atmospheric. A third method (8), developed in 1967, prepares very low water-demand α-hemihydrate by autoclaving powdered gypsum in a slurry. A crystal-modifying substance such as succinic acid or malic acid is added to the slurry in the autoclave to produce large squat crystals.

Anhydrite. In addition to kettle calcination (Fig. 1), soluble anhydrite is commercially manufactured in a variety of forms, from fine powders to granules 4.76 mm (4 mesh) in size, by low temperature dehydration of gypsum.

Insoluble anhydrite is manufactured commercially by several methods. Where large rock gypsum is the starting material, beehive kilns are used and 24-h processing times are not unusual. Rotary calciners or traveling grates are often used for small rock feed. Fine-ground gypsum is calcined to the insoluble form in flash calciners. Temperature control is somewhat critical in all methods; low temperatures result in soluble anhydrite being present and too high temperatures dissociate the $CaSO_4$ into CaO and oxides of sulfur.

By-Product Calcium Sulfate. There are many industrial chemical processes that produce by-product calcium sulfate in one of its forms. Whereas the most common is the neutralization of spent sulfuric acid, many of those processes do not produce a commercially useful by-product because of contaminants, particle size, or volume produced. There are, however, six chemical processes that do produce sufficient volume to have potential commercial value. Each is named after its chemical process.

Desulphogypsum or FGD-gypsum are the two names commonly given to the by-product gypsum produced by scrubbing sulfur dioxide out of flue gases (see SULFUR REMOVAL AND RECOVERY). There are three general types of scrubbing processes that produce by-product gypsum: limestone, lime, and dual or double alkali.

The process for limestone scrubbing can be generally described by *Absorption*

$$SO_2 + H_2O \rightarrow H_2SO_3$$

Crystallization

$$H_2SO_3 + CaCO_3 \rightarrow CaSO_3 + CO_2 + H_2O$$

Oxidation

$$2\,CaSO_3 + O_2 + 4\,H_2O \rightarrow 2\,CaSO_4{\cdot}2H_2O$$

There are several lime-scrubbing processes being marketed. The generalized process is described by *Absorption*

$$2\,Ca(OH)_2 + 2\,SO_2 \rightarrow 2\,CaSO_3\cdot\frac{1}{2}H_2O + H_2O$$

Oxidation/crystallization

$$2\,CaSO_3\cdot\frac{1}{2}H_2O + O_2 + 3\,H_2O \rightarrow 2\,CaSO_4\cdot 2H_2O(s)$$

In the dual or double alkali process, an alkali salt that is considerably more soluble in water than limestone is used. The alkali salt is then regenerated using a second alkali, $CaCO_3$. There are several alkalies used in the absorber; the most common are magnesium sulfite, sodium sulfite, and ammonium sulfite. A typical process using magnesium sulfite is *Absorption*

$$MgSO_3 + H_2O + SO_2 \rightarrow Mg^{+2} + 2\,HSO_3$$

Oxidation/crystallization

$$2\,HSO_3 + 2\,CaCO_3 \rightarrow 2\,CaSO_3\cdot\frac{1}{2}H_2O + 2\,CO_2 + \frac{1}{2}O_2$$

$$2\,CaSO_3\cdot\frac{1}{2}H_2O + O_2 + 3\,H_2O \rightarrow 2\,CaSO_4\cdot 2H_2O(s)$$

Of all the by-product gypsums from chemical processes, desulphogypsum from coal-fired electric power utility plants has the greatest commercial potential because electric power plants are numerous and many are located near large population centers where there would be a ready market for by-product gypsum wallboard products (see COAL CONVERSION PROCESSES; POWER GENERATION). Utilization of gypsum is dependent on economically removing deleterious chemicals, namely excess chlorides, water-soluble sodium and magnesium, and unoxidized calcium sulfite.

By-product gypsum made by neutralizing waste sulfuric acid from the sulfate process used to manufacture titanium oxide pigment is called titanogypsum (see TITANIUM COMPOUNDS, INORGANIC). This is commonly a two-industry process in that iron-rich ilmenite ore is first processed to obtain iron and the resulting slag is sold to the TiO_2 producers. There are a few locations where titanogypsum is produced in large enough quantities to be considered for commercial use. Limitations are the iron compound contaminants and their average particle size. Titanogypsum has become the second most important source of commercial by-product gypsum after desulphogypsum in the United States.

Phosphogypsum *[13397-24-5]* is the name given to the by-product gypsum residue when phosphate ore is acidulated to extract phosphoric acid. There are several processes commercially used. All of them digest or acidulate tri-calcium phosphate.

$$Ca_3(PO_4)_2 + 3\,H_2SO_4 + 6\,H_2O \rightarrow H_3PO_4 + 3\,CaSO_4\cdot 2H_2O$$

Processing techniques vary by means of precipitation. In the United States, environmental considerations render by-product gypsum from all of the processes inappropriate for the building materials industry. Radon and daughter radionuclides are retained in the by-product residue after acidulation as is the heavy metal cadmium (see HELIUM GROUP GASES; CADMIUM AND CADMIUM ALLOYS). Phosphogypsum's commercial use in the gypsum wallboard industry in Europe and Japan has diminished as desulphogypsum has become more available.

Fluorogypsum is the name ascribed to by-product gypsum from fluorspar acidulation to produce hydrofluoric acid. The chemical reaction

$$CaF_2 + H_2SO_4 \xrightarrow{\Delta} CaSO_4 + 2\,HF(g)$$

produces anhydrite. Over a period of time, the anhydrite converts to gypsum. Contaminants in fluorogypsum, especially the heavy metal beryllium, render fluorogypsum a better road metal, ie, roadbed material, for which it is used, than a building materials product.

Citrogypsum and borogypsum are named after the respective processes and produce sizeable quantities of by-product gypsum in certain locations. However, contaminants preclude commercial use in the gypsum wallboard industry.

Uses

Uncalcined Gypsum and Anhydrite. Calcium sulfate, generally in the form of gypsum, is added to Portland cement (qv) clinker to stop the rapid reaction of calcium aluminates (flash set) (see ALUMINUM COMPOUNDS, ALUMINUM OXIDE ALUMINA). Also, gypsum accelerates strength development. For this reason, gypsum is more properly termed a set regulator, rather than a retarder, for Portland cement. Used in proper amounts it also minimizes volume change. Normal gypsum addition to clinker is 5–6 wt %. Another notable use of uncalcined gypsum is in agricultural soil treatment wherein it is commonly called land plaster. For this use it is finely ground.

Calcined Anhydrite. Soluble anhydrite, or second-settle stucco, has physical properties similar to those of gypsum plaster. It hydrates to the dihydrate rapidly in water. Its outstanding property is its extreme affinity for any moisture, which makes it a very efficient drying agent (see DESICCANTS). In ambient moisture-laden air, it readily hydrates to hemihydrate. Soluble anhydrite, under the trade name Drierite, is widely used as a desiccant in the laboratory and in industry. A small amount is also used as an insecticide carrier. Small amounts of soluble anhydrite are unintentionally produced in most commercial calciners during hemihydrate production.

Keenes Cement is produced from calcined anhydrite (dead-burned), finely ground and intermixed with special accelerator(s). Although the volume of its use has declined greatly since the 1960s, it is available for job-site mixing with hydrated lime as a composite, hand-finished plaster applied generally over an aggregated, gypsum-base (conventional) plaster.

Hemihydrate. The ability of plaster of Paris to readily revert to the dihydrate form and harden when mixed with water is the basis for its many uses. Of equal significance is the ability to control the time of rehydration in the range of two minutes to over eight hours through additions of retarders, accelerators, and or stabilizers. Other favorable properties include its fire resistance, excellent thermal and hydrometric dimensional stability, good compressive strength, and neutral pH.

Upon setting, gypsum expands slightly and this property can be used to reproduce the finest detail, down to ca 1 μm, as is done in certain dental and jewelry castings employing the lost wax process. Normal linear expansion upon setting of gypsum plaster is 0.2–0.3%, but by using additives expansion may be controlled for special uses in the range of from 0.03 to 1.2%.

The calcination procedures and processing techniques produce a family of base stuccos best described by the amount of water, in wt %, of the plaster, which must be added when mixing to obtain standard fluidity. The range of fluidity permits casting neat plaster in the dry range of specific gravity of about 0.85–1.8 and consequent dry compressive strength of about 3.5–70 MPa (35–700 atm). Frequently these stuccos are formulated with set and expansion control additives as well as many other materials to meet the needs of a particular application. Properties that limit gypsum plaster usage include plastic flow underload, which is increased under humid conditions, strength loss in a humid atmosphere, and dissolution and erosion in water. Thus gypsum is not normally used for permanent performance structurally or in exposed, exterior locations. To prevent long-term calcination, gypsum products should not be used where temperatures exceed 45°C.

The largest single use of calcined gypsum in North America is in the production of gypsum board. Gypsum wallboard replaced plaster in the United States during the 1960s as the main wall cladding material. During that same time period, new veneer plaster systems were developed as an alternative to gypsum board (drywall) and the classic plastering systems, all of which are specified in building construction (see BUILDING MATERIALS, SURVEY). The veneer plasters are highly proprietary and specially formulated composites that provide good wear-resistant interior wall and ceiling surfaces. They are applied on the construction site either by a one- or two-coat procedure at thicknesses of about 0.19–0.32 cm.

Molding plasters have been used for centuries to form cornices, columns, decorative moldings, and other building interior features. Molding plaster

is a good utility plaster where expansion control, high hardness, and strength are not needed. Its miscellaneous uses are numerous. Art plasters are essentially molding plasters modified to increase surface hardness, chip resistance, and to reduce paint absorption of casts made from this material. Orthopedic plasters are used by hospitals and clinics for all types of orthopedic cast work.

A moderate amount of plaster is used in making impressions and casting molds for bridges, etc, by dental laboratories. Both α- and β-plasters are used by the dental trade (see DENTAL MATERIALS). The α-plasters are also tailored to meet the needs of modern industrial tooling, where they are used for master patterns, models, mock-ups, working patterns, match plates, etc. They are the accepted material because their use results in great time and labor savings, as well as excellent accuracy and stability of cast dimensions. Also the material is adaptable to intricate, irregular shapes, complex intersections, and quick modification.

Shipping and Specifications

Gypsum and gypsum products are bulky and relatively low in cost. In North America, factors of varying regional supply and demand for building products not withstanding, the normal economic overland shipping range is about 500 km. For overland shipments there has been a steady shift, starting in the 1950s, from rail to motor transport. In some cases, truck shipments are made from plants directly to building construction sites. For continental coastal and lake region markets, crude gypsum is most often transported in specially designed, rapid unloading ships that deliver from quarries to plant sites where the gypsum is then processed into finished products. During the 1980s, there were reports of increased intercontinental trade in both crude gypsum ore and manufactured goods.

Formulated plasters utilizing specially processed calcined gypsum are packaged in multi-ply paper bags having moisture vapor-resistant liners. This type of packaging protects the contents from airborne moisture keeping the plaster more stable with respect to setting time and mixing water demand over longer periods of warehousing. Manufactured board products are most often bundled, two pieces face to face, stacked in units for transport to dealers' yards, and reshipped to individual job sites as construction schedules dictate. Specialized, labor saving, power driven handling equipment has been developed for stocking boards on construction sites. The ASTM specifications for gypsum and gypsum products are given in Table 3.

Table 3. ASTM Gypsum and Gypsum Product Specifications

ASTM method	Materials
	Gypsum and gypsum plasters
C22-91	Gypsum
C28-91	Gypsum Plasters
C35-89a	Inorganic Aggregates For Use In Gypsum Plaster
C59-91	Gypsum Casting and Molding Plaster
C61-91	Gypsum Keene's Cement
C317-91	Gypsum Concrete
C587-91	Gypsum Veneer Plaster
	Test methods
C265-91	Calcium Sulfate in Hydrated Portland Cement
C471-91	Chemical Analysis of Gypsum and Gypsum Products
C472-90a	Physical Testing of Gypsum Plasters, etc
	Gypsum board products
C36-91	Wallboard (general)
C37-91	Lath (base for plaster)
C79-91	Sheathing
C442-91	Backing Board and Coreboard
C588-91	Base for Veneer Plasters
C630-91	Water-Resistant Backing Board
C931-91	Exterior Soffit Board
C960-91	Predecorated Board
	Test method
C473-87a	Physical Testing of Gypsum Board Products

Production and Trade

Crude gypsum is the principal form of calcium sulfate shipped in international trade, although the 1980s saw an increase in the volume of fabricated products moved across international borders. Tables 4 and 5 summarize production and trade of gypsum materials for the United States, Canada, Mexico, and other regions of the world. The United States remains both a leading producer and importer of gypsum. In 1989, over 8,400,000 metric tons of crude gypsum were imported into the United States; 67.5% from Canada, 25.3% from Mexico, and the remainder, in order of decreasing quantity from Spain, Australia, China, Morocco, The Dominican Republic, Germany (FDR), and Japan.

Table 4. World Production of Gypsum, 10^3 t[a]

Country	Year 1986	Year 1990[b]
Argentina	462	399
Australia	1,672	1,797
Austria[c]	703	635
Brazil (direct sales plus beneficiated)	629	654
Bulgaria	395	495
Canada (shipments)[c]	8,809	8,207
China	6,536	7,989
Czechoslovakia	743	794
Egypt	906	1,307
France[c]	5,263	5,628
Germany		
eastern states	340	300
western states (marketable)[c]	1,897	1,797
Greece	499	454
India	1,641	1,598

Iran	8,118	7,989
Italy	1,246	1,253
Japan	6,355	6,355
Mexico	4,236	6,005
Morocco	454	454
Pakistan	373	472
Poland[c]	1,108	1,108
Romania	1,598	1,498
Russia	4,603	4,721
Saudi Arabia	373	375
South Africa, Republic of	405	385
Spain	5,066	4,993
Thailand	1,667	5,757
United Kingdom[c]	3,418	3,994
United States[d]	13,983	14,893
Yugoslavia	596	554
other countries	4,195	4,884
Total	*88,289*	*97,744*

[a] Ref. 9.

[b] Estimated.

[c] Includes anhydrite.

[d] Excludes by-product gypsum.

Table 5. United States' Crude Gypsum, 10^3 t[a,b]

Year	Consumption[c]	Production	Imports[d]	Exports[d]	Inventories[e]	Representative price $ t[f]
1976	16,499	10,866	5,652	19	1,375	5.51
1980	17,899	11,225	6,680	6	1,492	9.18
1984	21,059	12,988	8,076	5	1,755	8.75
1988	23,673	14,875	8,780	5	1,973	7.34
1989[g]	22,404	14,059	8,439	98	1,867	6.62
1990	22,698	14,893	7,921	117	1,843	5.51

[a] Ref. 10.

[b] Excludes by-product gypsum.

[c] Consumption includes sold or used, minus exports. Data on quantities sold or used is from the quarterly gypsum canvasses of the nongypsum board producers, annual canvasses of all producers, and from data furnished by the Gypsum Association.

[d] Imports and exports are from the Bureau of Census.

[e] Inventories estimated from consumption.

[f] The representative price is the company-reported value per metric ton, fob mine or plant.

[g] Preliminary data.

In 1989, 4,689,000 metric tons of uncalcined gypsum was sold or used; 3,229,000 metric tons for use in Portland cement and the remainder for agriculture and miscellaneous uses. About 17,778,000 metric tons of calcined material was used to produce 1.9 million square meters of board products. Over one million square meters of this material was regular board and about 560,000 m^2 was Type X board.

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CALCIUM MAGNESIUM ACETATE.

See ACETIC ACID AND DEERIVATIVES, ACETIC ACID; CALCIUM COMPOUNDS, SURVEY.

CALIFORNIUM.

See ACTINIDES AND TRANSACTINIDES.

CALKING AND SEALING COMPOSITIONS.

See SEALANTS.

CALORIZING.

See METALLIC COATINGS.

CAMPHOR.

See TERPENOIDS.

CANCER CHEMOTHERAPY.

See CHEMOTHERAPEUTICS, ANTICANCER.

CANDLES.

See WAXES.

CAPACITOR FLUIDS.

See HEAT EXCHANGE TECHNOLOGY.

CAPRIC ACID.

See CARBOXYLIC ACIDS.

CAPROIC ACID.

See CARBOXYLIC ACIDS.

CAPROLACTAM

Caprolactam *[105-60-2]* (2-oxohexamethylenimine, hexahydro-2*H*-azepin-2-one) is one of the most widely used chemical intermediates. However, almost all of the annual production of 3.0×10^6 t is consumed as the monomer for nylon-6 fibers and plastics (see FIBERS SURVEY; POLYAMIDES, PLASTICS). Cyclohexanone, which is the most common organic precursor of caprolactam, is made from benzene by either phenol hydrogenation or cyclohexane oxidation (see CYCLOHEXANOL AND CYCLOHEXANONE). Reaction with ammonia-derived hydroxylamine forms cyclohexanone oxime, which undergoes molecular rearrangement to the seven-membered ring ε-caprolactam.

Caprolactam was first successfully polymerized to Perlon in 1938 by I. G. Farben and the associated technology was acquired as a part of postwar reparations by the Western Allies and the former USSR (1). By 1965 other countries, eg, Italy and Japan, had developed their own caprolactam processes, each involving nitrosation of an aliphatic ring.

In the United States in 1992, annual caprolactam production was about 0.6 × 10^6 t: 45% by Allied-Signal, Inc.; 30%, BASF; 25%, DSM.

Physical Properties

Caprolactam, mol wt 113.16, is a white, hygroscopic, crystalline solid at ambient temperature, with a characteristic odor. It is very soluble in water and in most common organic solvents and is sparingly soluble in high molecular weight aliphatic hydrocarbons. Molten caprolactam is a powerful solvent for polar and nonpolar organic chemicals. Selected physical properties and solubilities of caprolactam are listed in Tables 1 and 2, respectively.

Table 1. Physical Properties of Caprolactam $CH_2(CH_2)_4CONH$

Properties	Values	References
melting point, °C	69.3	2
density (at 77°C), g/cm^3	1.02	3
bulk density, kg/m^3	600–700	3,4
vapor pressure, kPa[a]		
at 270°C	100.6	5
at 180°C	8.13	5
at 150°C	2.62	5
at 130°C	1.10	5
at 115°C	0.53	5
at 70°C	0.032	5
at 25°C (solid)	0.0004	5
refractive index		
at 40°C	1.4935	3,6
at 31°C	1.4965	
viscosity, mPa·s, (=cP)		
at 70°C	12.3	4
at 78°C	9	3
at 80°C	8.5	4
at 90°C	6.1	4
specific heat, J/(kg·K)[b]		
solid		
at 25°C	1380	3
at 28.5°C	1340	4
at 35°C	1420	3
liquid		
at 70°C	2117	3
at 80°C	2269	4
at 110°C	2412	4
at 140°C	2504	4
at 178°C	2608	4
vapor		
at 100°C	1640	7
thermal conductivity, W/(m·K)	0.169	7
heat of fusion, J/g[c]	135.9	8
heat of vaporization at 80°C, J/g[c]	580	5
heat of combustion (liquid at 25°C), J/g[c]	31,900	2,7
heat of formation (liquid at 25°C), J/g[c]	2,840	2,7
flash point (closed cup), °C	125	7,9
fire point, °C	140	7,9

[a] To convert kPa to mm Hg, multiply by 7.5.

[b] To convert J/(kg·K) to cal/(g·°C), divide by 4184.

[c] To convert J to cal, divide by 4.184.

Table 2. Solubility of Caprolactam[a]

Solvent	Temperature, °C	Solubility, g/100 g solvent
water	25	525
1,2,3-trichloropropane	18	95
1,2-dichloroethane	18	95
1,4-dichlorobutane	10	85
1,3-dichloropropane	18	90
cyclohexane	20	2
	30	2.4
	40	7.3
	50	22.7
toluene	20	35
	30	58
	40	104
	50	198
cyclohexanol	20	82
	30	111
	40	154

	50	223
cyclohexanone	20	53
	30	73
	40	120
	50	214
methyl ethyl ketone	20	53
	30	84
	40	145
	50	280
ethyl acetate	20	32
	30	50
	40	94
	50	195
p-xylene	20	16
	30	37
	40	75
	50	163

[a] Refs. 3 and 7.

The vapor pressure values have been calculated at the indicated temperatures using the relationship derived from experimental data at Pennsylvania State University, and a critical review of literature references (5). This study is a part of the effort by the American Institute of Chemical Engineers (AIChE) to obtain accurate data through their Design Institute for Physical Property Data (DIPPR).

The vapor pressure for the solid at 25°C has been calculated from the value for the liquid at 70°C and the heats of vaporization and fusion using the Clausius-Clapeyron relationship.

The low melting point of caprolactam and its stability and low viscosity form the basis for commercial transportation practice: caprolactam is handled as a liquid in insulated tank cars or trucks.

The infrared spectrum of caprolactam has been given (3). Melting point data for the caprolactam–water system, as shown in Figure 1, are indicative of successful purification of caprolactam by crystallization from aqueous solution; such purification is very effective for separating and rejecting polar impurities.

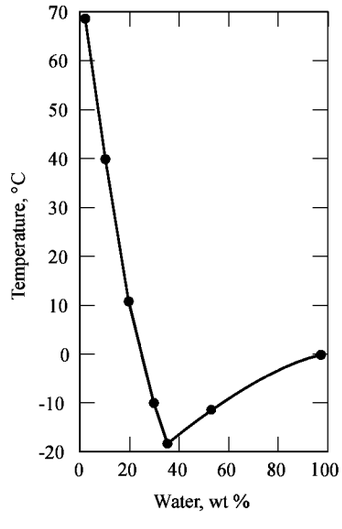


Fig. 1. Melting point data for the caprolactam–water system.

Reactions

Caprolactam is an amide and, therefore, undergoes the reactions of this class of compounds. It can be hydrolyzed, *N*-alkylated, *O*-alkylated, nitrosated, halogenated, and subjected to many other reactions (3). Caprolactam is readily converted to high molecular weight, linear nylon-6 polymers. Through a complex series of reactions, caprolactam can be converted to the biologically and nutritionally essential amino acid L-lysine (10) (see AMINO ACIDS).

Manufacture

All commercial processes for the manufacture of caprolactam are based on either toluene or benzene, each of which occurs in refinery BTX-extract streams (see BTX PROCESSING). Alkylation of benzene with propylene yields cumene (qv), which is a source of phenol and acetone; ca 10% of U.S. phenol is converted to caprolactam. Purified benzene can be hydrogenated over platinum catalyst to cyclohexane; nearly all of the latter is used in the manufacture of nylon-6 and nylon-6,6 chemical intermediates. A block diagram of the five main process routes to caprolactam from basic raw materials, eg, hydrogen (which is usually prepared from natural gas) and sulfur, is given in Figure 2.

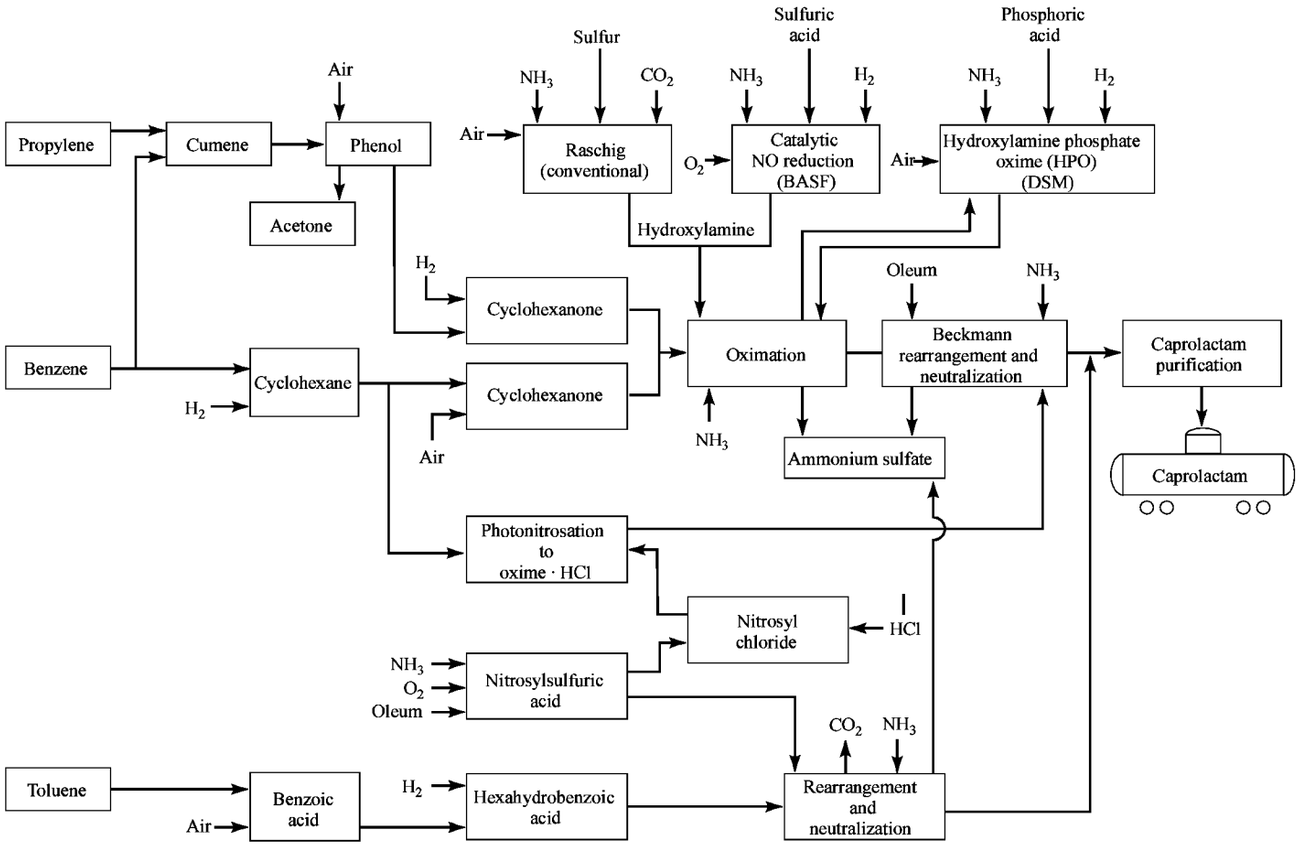


Fig. 2. Caprolactam processes.

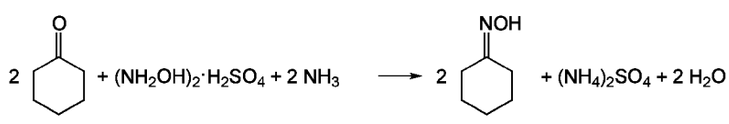
Allied-Signal Process. Cyclohexanone *[108-94-1]* is produced in 98% yield at 95% conversion by liquid-phase catalytic hydrogenation of phenol. Hydroxylamine sulfate is produced in aqueous solution by the conventional Raschig process, wherein NO_x from the catalytic air oxidation of ammonia is absorbed in ammonium carbonate solution as ammonium nitrite (eq. 1). The latter is reduced with sulfur dioxide to hydroxylamine disulfonate (eq. 2), which is hydrolyzed to acidic hydroxylamine sulfate solution (eq. 3).

$$N_2O + (NH_4)_2CO_3 \rightarrow 2\,NH_4NO_2 + CO_2 \tag{1}$$

$$2\,NH_4NO_2 + 4\,SO_2 + 2\,NH_3 + 2\,H_2O \rightarrow 2\,HON(SO_3NH_4)_2 \tag{2}$$

$$2\,HON(SO_3NH_4)_2 + 4\,H_2O \rightarrow (NH_2OH)_2{\cdot}H_2SO_4 + 2\,(NH_4)_2SO_4 + H_2SO_4 \tag{3}$$

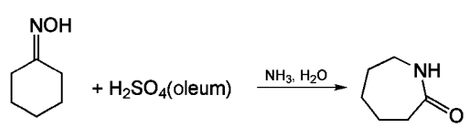
Simultaneous neutralization and reaction produce cyclohexanone oxime *[100-64-1]* (eq. 4).



(4)

Concentrations are controlled to yield a molten oxime product layer and a saturated (ca 40 wt %) ammonium sulfate solution; ca 125% (theoretical) ammonium sulfate or 2.9 kg kg caprolactam is produced as a result of side reactions in the hydroxylamine synthesis.

Cyclohexanone oxime is converted quantitatively to caprolactam by Beckmann rearrangement in the presence of oleum, which is of sufficient strength to consume the several percent water in the molten oxime. The reaction mass is neutralized with aqueous ammonia to a crude caprolactam layer and a saturated solution of ammonium sulfate. Approximately 1.5 kg of the total 4.4 kg ammonium sulfate per kilogram of caprolactam is produced in this step. Purification is by multistage vacuum crystallization from aqueous solution in nearly quantitative yield.



BASF. In the Badische process, cyclohexanone is produced by liquid-phase catalytic air oxidation of cyclohexane to KA oil, which is a mixture of cyclohexanone and cyclohexanol, and is followed by vapor-phase catalytic dehydrogenation of the cyclohexanol in the mixture. Overall yields range from 75% at 10% cyclohexane conversion to 80% at 5% cyclohexane conversion.

Hydroxylamine sulfate is produced by direct hydrogen reduction of nitric oxide over platinum catalyst in the presence of sulfuric acid. Only 0.9 kg ammonium sulfate is produced per kilogram of caprolactam, but at the expense of hydrogen consumption (11). A concentrated nitric oxide stream is obtained by catalytic oxidation of ammonia with oxygen. Steam is used as a diluent in order to avoid operating within the explosive limits for the system. The oxidation is followed by condensation of the steam. The net reaction is

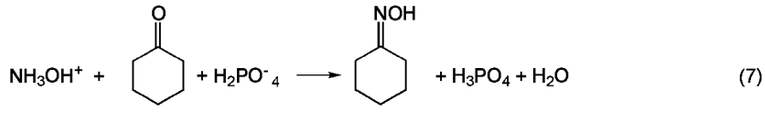
$$2\,NO + 3\,H_2 + H_2SO_4 \rightarrow (NH_2OH)_2{\cdot}H_2SO_4$$

The formation of oxime and rearrangement to caprolactam are conventional. The rearrangement produces 1.5 kg of the total 2.4 kg by-product ammonium sulfate per kilogram of caprolactam. Purification is accomplished by vacuum distillation. A similar caprolactam process is offered by Inventa (11).

Dutch State Mines (Stamicarbon). Vapor-phase, catalytic hydrogenation of phenol to cyclohexanone over palladium on alumina, licensed by Stamicarbon, the engineering subsidiary of DSM, gives a 95% yield at high conversion plus an additional 3% by dehydrogenation of coproduct cyclohexanol over a copper catalyst. Cyclohexane oxidation, an alternative route to cyclohexanone, is used in the United States and in Asia by DSM. A cyclohexane vapor-cloud explosion occurred in 1975 at a co-owned DSM plant in Flixborough, UK (12); the plant was rebuilt but later closed. In addition to the conventional Raschig process for hydroxylamine, DSM has developed a hydroxylamine phosphate–oxime (HPO) process for cyclohexanone oxime; no by-product ammonium sulfate is produced. Catalytic ammonia oxidation is followed by absorption of NO_x in a buffered aqueous phosphoric acid solution (eq. 5), hydrogen reduction over palladium catalyst (eq. 6), and two-phase reaction with cyclohexanone in toluene solvent to an oxime–toluene phase and a recycled aqueous phase (eq. 7) (13).

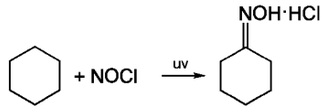
$$HNO_3 + H_2PO_4^- \rightarrow NO_3^- + H_3PO_4 \tag{5}$$

$$NO_3^- + 2\,H_3PO_4 + 3\,H_2 \rightarrow NH_3OH^+ + 2\,H_2PO_4^- + 2\,H_2O \tag{6}$$

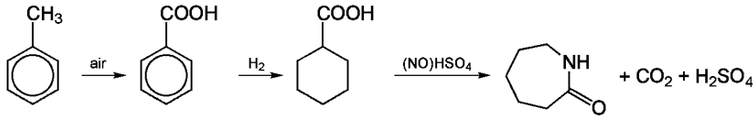


The oxime is converted to caprolactam by Beckmann rearrangement; neutralization with ammonia gives ca 1.8 kg ammonium sulfate per kilogram of caprolactam. Purification is by vacuum distillation. A no-sulfate, extraction process has been described, but incineration of the ammonium bisulfate recovers only sulfur values and it is not practiced commercially (14).

Toray. The photonitrosation of cyclohexane or PNC process results in the direct conversion of cyclohexane to cyclohexanone oxime hydrochloride by reaction with nitrosyl chloride in the presence of uv light (15) (see PHOTOCHEMICAL TECHNOLOGY). Beckmann rearrangement of the cyclohexanone oxime hydrochloride in oleum results in the evolution of HCl, which is recycled to form NOCl by reaction with nitrosylsulfuric acid. The latter is produced by conventional absorption of NO_x from ammonia oxidation in oleum. Neutralization of the rearrangement mass with ammonia yields 1.7 kg ammonium sulfate per kilogram of caprolactam. Purification is by vacuum distillation. The novel chemistry is as follows:



Snia Viscosa. Catalytic air oxidation of toluene gives benzoic acid (qv) in ca 90% yield. The benzoic acid is hydrogenated over a palladium catalyst to cyclohexanecarboxylic acid *[98-89-5]*. This is converted directly to crude caprolactam by nitrosation with nitrosylsulfuric acid, which is produced by conventional absorption of NO_x in oleum. Normally, the reaction mass is neutralized with ammonia to form 4 kg ammonium sulfate per kilogram of caprolactam (16). In a no-sulfate version of the process, the reaction mass is diluted with water and is extracted with an alkylphenol solvent. The aqueous phase is decomposed by thermal means for recovery of sulfur dioxide, which is recycled (17). The basic process chemistry is as follows:



Purification involves chemical treatment and vacuum distillation.

Economic Aspects

Estimated worldwide annual caprolactam production capacities are shown in Table 3. New plant construction is planned in Korea, Taiwan, India, China, and Indonesia. Total new capacity over the next 10 years could exceed 500,000 tons per year.

Table 3. Estimated Worldwide Annual Production Capacity of Caprolactam[a]

		Annual capacity, 10^3 t			
Producer	Location	1980	1985	1990	1995
United States					
Allied-Signal	Hopewell, Va.	220	250	300	320
BASF	Freeport, Tex.	160	160	180	225
DSM	Augusta, Ga.	170	180	160	160
Subtotal		*550*	*590*	*640*	*705*
Western Europe					
BASF	Antwerp, Belgium	140	140	140	140
	Ludwigshafen, Germany	140	140	140	140
Bayer	Antwerp, Belgium	90	90	110	110
	Uerdingen, Germany	60	60		
DSM	Geleen, The Netherlands	200	200	230	230
Nypro	Flixborough, UK	65			
SNIA Montedipe	Torviscosa, Italy	15	15	15	15
	Manfredonia, Italy	80	80	100	100
	Porto Marghera, Italy	75	75	80	80
other	Spain, Switzerland	35	35	45	45
Subtotal		*900*	*835*	*860*	*860*
Eastern Europe					
Polimex	Poland	110	110	110	110
Technashimport	Russia	550	550	550	550
Chemopetrol	Czechoslovakia	45	70	70	70
VEB Leunawerke	Germany	60	60	75	75
other	Romania, Bulgaria, Hungary, Yugoslavia	80	90	90	90

Subtotal		*845*	*880*	*895*	*895*
Japan					
Japan Lactam (Sumitomo)	Nihama, Japan	60	60	75	75
Mitsubishi Chem.	Kurosaki, Japan	80	80	100	100
Toray Ind.	Nagoya, Japan	130	130	145	145
Ube Ind.	Ube Sakai, Japan	160	160	180	180
Subtotal		*430*	*430*	*500*	*500*
Latin America					
Univex	Salamanca, Mexico	45	45	70	70
Nitrocarbono	Camacari, Brazil	35	55	55	55
Monomeros	Colombia	25	25	25	25
Subtotal		*105*	*125*	*150*	*150*
Asia					
Hanook Caprolactam	Ulsan, Korea	40	80	80	80
Hanhua Caprolactam	Korea				80
Chung Tai	Taipei, Taiwan	90	100	110	110
FCFC	Taiwan				120
other	China, India, Turkey, Indonesia, Thailand	55	55	100	300
Subtotal		*185*	*235*	*290*	*690*
Total		*3015*	*3095*	*3335*	*3800*

[a] Ref. 18.

Worldwide caprolactam demand increased about 2% per year during the 1980s, and similar growth is expected into the 1990s. Because of the new capacity coming on-stream in the Far East, production will stay basically flat in the United States and in Europe.

The caprolactam prices shown in Table 4 are for large contracts of molten material. Flaked material is sold in bags, either in small lots or for export, and costs ca $0.10 kg more than the molten product. Exports normally have risen during periods of recession in the United States, eg, 1970, 1975, 1980, and 1990.

Table 4. U.S. Caprolactam Production, Price, and Exports[a]

			Exports	
Year	Production, 10^3 t	Price (molten), $ kg	10^3 t	$ kg
1963	85	1.01		
1965	131	0.91		
1967	149	0.73	7.0	0.48
1969	218	0.54	18	0.40
1971	261	0.54	18	0.42
1973	298	0.54	8.6	0.48
1975	324	1.07	17	0.87
1977	393	1.11	9.5	0.88
1979	429	1.42	16	1.22
1980	412	1.69	30	1.65
1981	422	1.85	24	1.43
1982	360	1.78	28	1.32
1983	440	1.74	12	1.32
1984	467	1.83	29	1.34
1985	495	1.96	28	1.30
1986	504	1.96	13	1.23
1987	526	2.01	34	1.43
1988	573	2.13	68	1.61
1989	596	2.22	66	1.56
1990[b]	610	2.10	75	1.90

[a] Refs. 19, 20.

[b] 1990 data, estimated.

DSM America produces caprolactam only for merchant sales, both domestic and foreign. BASF is a customer, following acquisition of Enka's United States fiber and plastics plants, and also a captive producer of caprolactam. Allied-Signal's production is primarily captive for nylon-6 fibers and plastics, but substantial amounts are supplied to the export market.

Specifications and Analysis

The main contaminant and its concentration in commercial caprolactam usually is water at <0.1 wt%. Anhydrous caprolactam is produced in small quantity for use in anionic polymerization processes. Commercial product of very high purity is required by the users, ie, the fibers and plastics producers, most of whom utilize technologically advanced processes that are sensitive to monomer quality.

Commercial specifications are listed in Table 5. There are differences in the methods used by producers to measure color and oxidizable impurities. Color is measured from aqueous solutions either as transmission of light of a certain wavelength or by visual comparison with standard solutions. Permanganate oxidizable impurities are determined by spectrophotometric measurement of manganese dioxide, which forms upon addition of potassium permanganate (21), or according to the time taken by a sample containing permanganate to match the color of a reference solution visually. Values of 10,000 s or greater are common. Generally, moisture is measured by Karl Fischer titration; bases or acids by titration; water insolubles, visually; and iron, spectrophotometrically as the *o*-phenanthroline complex. Residual cyclohexanone oxime is measured colorimetrically after undergoing hydrolysis to hydroxylamine, oxidation by iodine to nitrous acid, diazotization of added sulfanilic acid, and formation of a colored compound by a coupling reaction of the diazonium salt with *N*-(1-naphthyl)ethylenediamine *[537-09-7]* (22). Chromatographic techniques have been used more recently. More details on methods of analysis, assay, and determination of impurities have been given (4,7).

Table 5. Caprolactam Specifications[a]

Property	Value

solidifying point (dry basis), °C	69.0 min
color, APHA	5 max
permanganate number, s	10,000 min
moisture, %	0.10 max
iron (as Fe), ppm	0.5 max
volatile bases (as NH_3), ppm	10 max
cyclohexanone oxime, ppm	10 max
free alkalinity, meq/kg	0 (neutral) min, 0.04 max

[a] Typical.

Flaked caprolactam has been shipped in multiwall, laminated paper bags with separable polyethylene liner, but single-ply polyethylene bags are becoming required for automatic equipment. The bags should be stored in a dry environment. Because molten caprolactam reacts readily with oxygen it is stored at ca 75°C, ie, just above the melting point, in insulated vessels and blanketed with nitrogen containing less than 5 ppm oxygen. Usually it is transported in aluminum or stainless-steel tank trailers or railroad cars.

Health and Safety Factors

Caprolactam has a low order of toxicity, as shown by the results of numerous and various toxicological tests in Table 6, and it presents no appreciable health hazard if it is handled properly. Prolonged exposure to dust or vapors causes irritation of eyes, mucous membranes, and skin; inhalation may cause irritation of the respiratory tissues. Skin contact, if prolonged, can lead to dermatosis causing a reddening and tightening of the skin, the appearance and sensation of which is similar to sunburn (24). A thorough wash with water, in which caprolactam is very soluble, or with soap and water, normally is sufficient to remove caprolactam from contaminated parts of the body.

Table 6. Biological Effects of Caprolactam

Lethal-dose data[a]	Value
LD_{50} (oral, rat), mg/kg	2140
LD_{Lo} (skin, rabbit), mg/kg	1410
LD_{Lo} (intraperitoneal, rat), mg/kg	900
LD_{Lo} (inhalation, human), ppm	100[b]
LD_{Lo} (subcutaneous, mouse), mg/kg	750
LD_{Lo} (subcutaneous, frog), mg/kg	2800

[a] Ref. 23.

[b] Irritant; olfactory threshold is 0.3 mg/m^3 (2).

Threshold limit values for caprolactam dust and vapor are 1 mg/m^3 and 4.3 ppm (20 mg/m^3), respectively, although the American Conference of Governmental Industrial Hygienists (ACGIH) has a notice of intended change (1991–1992) of 1 mg/m^3 for dust and 5 ppm (23 mg/m^3) for vapor with short-term exposure limits (STELs) of 3 mg/m^3 and 10 ppm for dust and vapor, respectively (time-weighted averages) (25). Caprolactam has been extensively tested for its mutagenic potential (26). Based on the overall weight of evidence, caprolactam would be considered nonmutagenic. It was also found to be noncarcinogenic in a National Cancer Institute bioassay using F344 rats and B6C3F1 mice (27). Caprolactam is not teratogenic (F344 rats and rabbits) (28). In a three-generation reproduction study conducted in rats, the only effects noted were slight body weight reductions in pups and dams at a high maternally toxic dose (10,000 ppm or 500 mg/kg/day in the diet). All pregnancy and fertility indexes were unaffected by treatment. Based on these results, caprolactam should not pose a hazard to reproduction and fertility and would not be considered a developmental toxicant (29).

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CAPRYLIC ACID.

See CARBOXYLIC ACIDS.

CARAMEL COLORS.

See COLORANTS FOR FOODS, DRUGS, AND COSMETICS.

CARBAMATES.

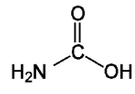
See POISONS, COMMERCIAL.

CARBAMIC ACID

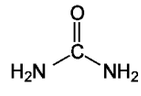
Carbamic acid *[463-77-4]*, NH_2COOH, is the hydrated form of isocyanic acid *[75-13-8]*, H—N═C═O. It is not known in the free state; hydrolysis rapidly gives ammonia and carbon dioxide.

$$HNCO + H_2O \rightarrow [H_2NCOOH] \rightarrow CO_2 + NH_3$$

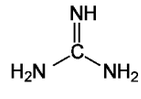
Carbamic acid is the monoamide of carbonic acid; the diamide is the well-known compound urea *[57-13-6]*, also called carbamide (see UREA). Guanidine *[113-00-8]* could be regarded as the amidine of carbamic acid (see CYANAMIDES).



carbamic acid



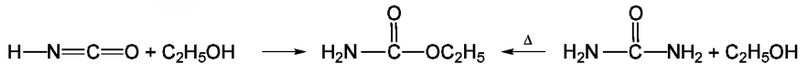
urea



guanidine

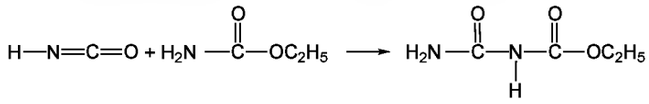
The acid chloride (chloroformamide *[463-72-9]*, "urea chloride"), NH_2COCl, and its salts have been prepared. Ammonium carbamate *[1111-78-0]*, can be obtained as a white crystalline solid by reaction of dry carbon dioxide and ammonia. It is an impurity in commercial ammonium carbonate *[506-87-6]* (see AMMONIUM COMPOUNDS). Esters of carbamic acid are quite stable. The best known is the ethyl ester usually called urethane *[51-79-6]*.

Alkyl carbamates (urethanes) are formed from reaction of alcohols with isocyanic acid or urea (see URETHANE POLYMERS).



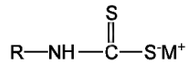
ethyl carbamate

With excess isocyanic acid, stable allophanates are formed (see CYANURIC AND ISOCYANURIC ACIDS).



ethyl allophanate

Salts of *N*-substituted dithiocarbamic acid *[594-07-0]* are used as fungicides (qv) and rubber vulcanization accelerators (see RUBBER CHEMICALS).



CARBAZOLE.

See AMINES, AMINES, AROMATIC DIARYLAMINES.

CARBIDES

Survey,
Cemented carbides,
Industrial hard carbides,
Calcium carbide,
Silicon carbide,

SURVEY

Carbon (qv) reacts with most elements of the periodic table to form a diverse group of compounds known as carbides, some of which are extremely important in technology. For example, calcium carbide, CaC_2, is a source of acetylene; silicon carbide, SiC, and boron carbide, B_4C, are used as abrasives (qv); tungsten carbide, WC, titanium carbide, TiC, and tantalum (niobium) carbide, TaC(NbC), find use as structural materials at extremely high temperatures or in corrosive atmospheres. Cementite, Fe_3C, and the multimetallic complexes (Co, W) C, $(Cr,Fe,Mo)_{23}C$, and $(Cr,Fe)_7C_3$, are the components in tool steels and Stellite-type alloys responsible for their hardness, wear, resistance, and excellent cutting performance. Numerous compounds also have potential applications as catalysts (see BORON COMPOUNDS; TUNGSTEN AND TUNGSTEN ALLOYS; TANTALUM AND TANTALUM COMPOUNDS; NIOBIUM AND NIOBIUM COMPOUNDS; TITANIUM AND TITANIUM COMPOUNDS).

Table 1 provides a survey of the most important and well-known binary compounds of carbon, according to position in the Periodic Table. These may be divided into four main groups: the saltlike, metallic, diamondlike, and volatile compounds of carbon (2), which have ionic, metallic, semiconductor, or covalent character, respectively. These and further subdivisions, used to characterize the compounds, are not rigid and there are a number of transitional cases. Whereas the members of Groups 2 and 3 are classified as saltlike carbides, some of the properties of Be_2C, eg, the very high degree of hardness, correspond to diamondlike carbides. Similarly, some monocarbides of Group 3, eg, scandium carbide, ScC, and uranium carbide, UC, as well as thorium carbide, ThC, have pronounced metallic characteristics.

Table . Binary Compounds of Carbon[a] and Their Position in the Periodic Table

	1(IA)	2(IIA)	3(IIIB)	4(IVB)	5(VB)	6(VIB)	7(VIIB)	8	9(VIII)	10	11(IB)	12(IIB)	13(IIIA)	14(IVA)	15(VA)	16(VIA)	17(VIIA)	18(O)
	H_2C_2												(1d) (1e) (3)	$M_x@C_{60}$ $M_x@C_{70}$ Ti_8C_{12}	(4)		H_4C H_xC_y	He
(1c)	Li_2C_2 (1b)	Be_2C											B_4C	C	$(NC)_2$	OC O_2C	F_4C	Ne
NaC_8 NaC_{16}	Na_2C_2	Mg_2C_3 MgC_2			(2a)			(2b)			(1b)		Al_4C_3 (1a)	SiC	P_2C_6 (2c)	S_2C	Cl_4C	Ar
KC_8 KC_{16} KC_{60}	K_2C_2	CaC_2	Sc_4C_3 ScC_{1-x} $Sc_{15}C_{19}$	TiC	V_2C^b V_4C_3 V_6C_5 V_8C_7 VC	$Cr_{23}C_6$ Cr_7C_3 Cr_3C_2	$Mn_{23}C_6$ $Mn_{15}C_4$ Mn_3C Mn_3S_2 Mn_7C_3	Fe_3C Fe_7C_3 Fe_2C	Co_2C Co_3C	Ni_3C	Cu_2C_2	ZnC_2	Ga	Ge	As_2C_6	Se_2C	Br_4C	Kr
RbC_8 RbC_{16} RbC_{60}	Rb_2C_2	SrC_2	YC_{1-x} $Y_{15}C_{19}$ YC_2	ZrC_{1-x}	Nb_2C^b Nb_3C_2 NbC Nb_4C_3	Mo_2C^b Mo_3C_2 MoC_{1-x} MoC	Te?	RuC (?)	Rh	Pd	Ag_2C_2	CdC_2	In	Sn	Sb	Te_2C	I_4C	Xe
CsC_8 CsC_{16}	Cs_2C_2	BaC_2	La_2C_3 LaC_2	HfC_{1-x}	Ta_2C^b Ta_3C_2 TaC Ta_4C_3	W_2C^b WC_{1-x} WC	$Re_{2-4}C$ ReC	OsC (?)	Ir	Pt	Au_2C_2	HgC_2	Ti	Pb	Bi	Po?	At?	Rn
	Fr?	Ra?	Ac?															
					Ce_2C_3 CeC_2	PrC Pr_2C_3 PrC_2	Nd_2C_3 NdC_2	PmC_2	Sm_3C Sm_2C_3 SmC_2	EuC_2	Gd_3C Gd_2C Gd_2C_3 GdC_2	Tb_3C Tb_2C_3 TbC_2	Dy_3C Dy_2C Dy_2C_3 DyC_2	Ho_3C Ho_2C Ho_2C_3 HoC_2	Er_3C Er_2C Er_2C_3 ErC_2	Tm_3C Tm_2C_3 TmC_2	Yb_3C Yb_2C_3 YbC_2	Lu_3C Lu_2C_3 LuC_2
					ThC ThC_2	PaC PaC_2	UC U_2C_3 UC_2	NpC Np_2C_3 NpC_2	PuC Pu_2C_3 PuC_2	Am?	Cm?	Bk?	Cf?	Ea?	Fm?	Mv?	No?	Lw?

(1a) Lanthanide Series

Actinide Series

[a] Numerical designations are (1a), saltlike carbides; (1b), acetylides; (1c), metal graphite compounds; (1d), metal fullerene compounds; (1e), metallo-carbohedrene clusters; (2a), metallic carbides of metals belonging to Groups 4–6 (IVB–VIB); (2b), metallic carbides of the iron metals, including Mn; (2c), metallic carbides of Group 5; (3), diamondlike carbides; and (4), volatile nonmetallic carbides. A line through the box, eg, ∅, indicates no carbide formation; however, there may be some solubility of carbon in the melt. A question mark, eg, Ac?, indicates the possibility of a carbide.

[b] Several modifications exist.

Carbides are generally stable at high temperatures and thus can be prepared by the direct reaction of carbon and metals or metal-like materials at high temperatures. However, this does not apply to the acetylides and the alkali metal–graphite compounds, which although being carbon compounds, fit only marginally in the category of carbides. Similarly, the large class of coordination compounds, ML_y, known as organometallics, are not typically considered carbides, even though the ligands, *L*, are attached to the metal center by metal–carbon bonds. The same applies to compounds such as $M_x@C_{60}$ or $M_x@C_{70}$, formed from diverse elements by association with fullerene structures (3) and metallo-carbohedrene clusters such as Ti_8C_{12}, in which metals are part of the polyhedral cage (4). The volatile compounds of carbon are also excluded.

Table 2 contains an alphabetical listing of carbides referred to in the text.

Table 2. Carbide Compounds

Carbide	CAS Registry Number	Formula
aluminum carbide (4:3)	*[1299-86-1]*	Al_4C_3
arsenic carbide (2:6)		As_2C

beryllium carbide	*[506-66-1]*	Be_2C
boron carbide (4:1)	*[12069-32-8]*	B_4C
calcium carbide (2:1)	*[75-20-7]*	CaC_2
chromium carbide	*[12011-60-8]*	CrC
chromium carbide (3:2)	*[12012-35-0]*	Cr_3C_2
chromium carbide (7:3)	*[12075-40-0]*	Cr_7C_3
chromium carbide (23:6)	*[12105-81-6]*	$Cr_{23}C$
cobalt carbide (3:1)	*[12011-59-5]*	Co_3C
cobalt tungsten carbide (6:6:1)	*[12538-07-7]*	Co W C
hafnium carbide	*[12069-85-1]*	HfC
iron carbide	*[12069-60-2]*	FeC
iron carbide (2:1)	*[12011-66-4]*	Fe_2C
iron carbide (3:1)	*[12011-67-5]*, *[12169-32-3]*	Fe_3C
iron carbide (5:2)	*[12127-45-6]*	Fe_5C_2
iron carbide (7:3)	*[12075-42-2]*	Fe_7C_3
iron carbide (23:6)	*[12012-72-5]*	$Fe_{23}C$
lanthanum carbide (1:2)	*[12071-15-7]*	LaC_2
manganese carbide (3:1)	*[12121-90-3]*	Mn_3C
manganese carbide (23:6)	*[12266-65-8]*	$Mn_{23}C$
magnesium carbide (1:2)	*[12122-46-2]*	MgC_2
magnesium carbide (2:3)	*[12151-74-5]*	Mg_2C_3
molybdenum carbide	*[12011-97-1]*	MoC
molybdenum carbide (2:1)	*[12069-89-5]*	Mo_2C
molybdenum carbide (23:6)	*[12152-15-7]*	$Mo_{23}C$
nickel carbide	*[12167-08-7]*	NiC
nickel carbide (3:1)	*[12012-02-1]*	Ni_3C
niobium carbide	*[12069-94-2]*	NbC
niobium carbide (2:1)	*[12011-99-3]*	Nb_2C
plutonium carbide	*[12070-03-0]*	PuC
plutonium carbide (2:3)	*[12076-56-1]*	Pu_2C_3
phosphorus carbide (2:6)		P_2C
scandium carbide	*[12012-14-5]*	ScC
silicon carbide	*[409-21-2]*	SiC
tantalum carbide	*[12070-06-3]*	TaC
tantalum carbide (2:1)	*[12070-07-4]*	Ta_2C
thorium carbide	*[12012-16-6]*	ThC
thorium carbide (1:2)	*[12071-31-7]*	ThC_2
titanium carbide	*[12070-08-5]*	TiC
tungsten carbide	*[12070-12-1]*	WC
tungsten carbide (2:1)	*[12070-13-2]*	W_2C
uranium carbide	*[12170-09-6]*	UC
uranium carbide (1:2)	*[12071-33-9]*	UC_2
uranium carbide (2:3)	*[12076-62-9]*	U_2C_3
vanadium carbide	*[12070-10-9]*	VC
vanadium carbide (2:1)	*[12012-17-8]*	V_2C
zirconium carbide	*[12020-14-3]*	ZrC

Saltlike Carbides. Almost all carbides of Groups 1–3 of the Periodic Table are saltlike. Beryllium carbide and Al_4C_3 may be considered as derivatives of methane (C^{4-} ion) and most carbides having C_2 groups, ie, C_2^{2-} ions, as derivatives of acetylene. This is supported to some extent by hydrolysis reactions:

$$Be_2C + 4\,H_2O \rightarrow 2\,Be(OH)_2 + CH_4$$

$$Al_4C_3 + 12\,H_2O \rightarrow 4\,Al(OH)_3 + 3\,CH_4$$

$$CaC_2 + 2\,H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

Propyne *[74-99-7]*, C_3H_4, is obtained from Mg_2C_3, which probably contains the C_3^{4-} ion, and it is also formed by thermal decomposition of MgC_2, with separation of graphite:

$$Mg_2C_3 + 4\,H_2O \rightarrow 2\,Mg(OH)_2 + CH_3C{\equiv}CH$$

If pure, the carbides of Groups 1 and 2 are characterized by their transparency and lack of conductivity. The carbides of Group 3, ie, Sc, Y, the lanthanides, and the actinides, are opaque. Some, depending on composition, show metallic luster and electroconductivity. The M^{2+} cation may exist in the MC_2 phases of this group, and the remaining valence electron apparently imparts partly metallic character to these compounds.

Uranium monocarbide, UC, which is important in nuclear reactor technology (see NUCLEAR REACTORS), is completely miscible with some of the metallic carbides of Groups 4 and 5 and also with ThC. Methane, ethylene, and hydrogen, as well as acetylene, are formed during the hydrolysis of the Group 3 carbides of varying composition, M_3C, MC, M_2C_3, and MC_2. The term acetylides, in the stricter sense, applies to carbides precipitated from aqueous solutions or from solutions in aqueous ammonia with acetylene (5). These compounds are metastablelike acetylides of Cu, Ag, Au, Na, K, Rb, Cs, Zn, Cd, Hg, Pd, Os, Ce, Al, Mg, etc, and require additives such as H_2, H_2O, NH_3, C_2H_2, or metal salts for stabilization. Thus it is doubtful whether they can be considered as pure metal–carbon compounds and described as carbides.

The alkali metal–graphite compounds formed by graphite absorption of the fused metals Na, K, Rb, and Cs, represent a special type of metal–carbon compound (6). These intercalation compounds having formulas MC_8 are brown; MC_{16} are gray; and MC_{60} are strongly graphitic.

Metallic Carbides. This class of compounds comprises the interstitial carbides of the transition metals of Groups 4–6 (see INDUSTRIAL,

INDUSTRIAL HARD CARBIDES) and the carbides of Groups 7–10. The metalloconductive carbides P_2C and As_2C are also included, as are some members of the lanthanide and actinide series.

Group 4–6 Metals. The early transition elements possess relatively large atomic radii and carbon resides in the interstitial cavities between metal atoms. In these interstitial carbides the metal atoms form relatively simple structures commonly found among pure metals: hexagonal closed-packed (hcp), face-centered cubic (fcc), and simple hexagonal (hex). In Groups 4 and 5 and some of the rare-earth carbides, the preferred structure is the B1 NaCl structure, where carbon occupies every octahedral site in an fcc arrangement of metal atoms. The resulting stoichiometry is MC, exemplified by TiC, ZrC, HfC, VC, NbC, TaC, UC, and PuC. There is often some carbon deficiency in these substances, which may either be disordered, as in the MC_{1-x} phases, or ordered, as in the compounds, V_8C_7, Nb_4C_3, etc. In Group 5 the stoichiometry M_2C appears, V_2C, Nb_2C, Ta_2C, which becomes most favorable for Group 6, Mo_2C, and W_2C. In this structure carbon randomly occupies half of the octahedral sites in an hcp arrangement of metal atoms. Again, substoichiometry may occur, as well as the formation of ordered vacancies. At high temperatures MoC_{1-x} and WC_{1-x} ($x \sim 0.5$) phases having an fcc arrangement of metal atoms are observed. Group 6 also shows retention of the MC stoichiometry, eg, MoC, WC, and (Mo, W)C. However, here carbon does not occupy the octahedral holes of the B1 structure, but rather the more spacious trigonal prismatic sites in a hex arrangement of metal atoms.

The Group 4–6 carbides are thermodynamically very stable, exhibiting high heats of formation, great hardness, elevated melting points, and resistance to hydrolysis by weak acids. At the same time, these compounds have values of electrical conductivity, Hall coefficients, magnetic susceptibility, and heat capacity in the range of metals (7).

Group 7–10 Metals. Carbides of the Group 7–10 metals are generally less stable than those of the earlier transition metals. The noble metals of the second and third row (Rh, Pd, Ir, Pt) do not form carbides at all. In moving to the right in the Periodic Table the size of the atoms decreases, and the metal lattice is no longer able to accommodate interstitial carbon atoms while maintaining close-packed or near close-packed metal atoms. Thus complex structures arise, for example, Mn_8C_3 is triclinic and Mn_4C is tetragonal, whereas Mn_3C, Fe_3C, and Co_3C are orthorhombic. The chromium carbides occupy an intermediate position in this respect, eg, Cr_3C_2 is also orthorhombic. Groups 7–10 compounds also differ markedly in chemical and physical behavior from the interstitial carbides. Hardness values and melting points are lower and chemical stability to mineral acids is also no longer apparent. However, these materials are still robust; these carbides are of technological importance as components in high speed tool steels and advanced alloys.

Properties and Nature of Bonding. The metallic carbides are interesting materials that combine the physical properties of ceramics (qv) with the electronic nature of metals. Thus they are hard and strong, but at the same time good conductors of heat and electricity.

The crystal structure and stoichiometry of these materials is determined from two contributions, geometric and electronic. The geometric factor is an empirical one (8): simple interstitial carbides, nitrides, borides, and hydrides are formed for small ratios of nonmetal to metal radii, eg, $r_X/r_M < 0.59$. When this ratio is larger than 0.59, as in the Group 7–10 metals, the structure becomes more complex to compensate for the loss of metal–metal interactions. Although there are minor exceptions, the Hägg rule provides a useful basis for predicting structure.

There is also an electronic factor that contributes to the bonding properties of the materials (9). The materials behave electronically as though the electron density increased by alloying. In forming carbide alloys, carbon combines its valence *sp* electrons with the metal *spd* band. Engel-Brewer theory may be used to predict the crystal structures of the materials based on the total number of valence *sp* electrons. Thus with increasing *sp* electrons, crystal structure is predicted to change from body-centered cubic (bcc) → hcp → fcc, as observed in the series Nb → Nb_2C → MoC_{1-x} or Ta → Ta_2C → WC_{1-x}. Increasing band occupancy is also indicated by the occurrence of a maximum in melting point for the Group 5 carbides as opposed to the Group 6 metals. Furthermore, increased metal to nonmetal stoichiometry, ie, MC → M_2C → M_3C, in moving to the right in the Periodic Table suggests rejection of carbon by the metal. This occurs from the filling of the antibonding portion of the electronic band.

Ideas on bonding have evolved considerably over the years (10). Early models considered bonding to arise from resonance between different covalent canonical forms. The hardness and brittleness of the compounds were attributed to the presence of directed covalent bonds, and the electrical conductivity to the existence of resonance structures. An opposing view, based on the high electronegativity of carbon compared to metals, held that the bonding was ionic in nature. This explained the refractory nature and the B1 NaCl structure of many of the compounds, but did not account for the instability of carbides beyond Group 6. The instability was explained by band structure models that suggested that in compounds of the late transition metals an antibonding portion of the *d*-band was being filled. This was consistent with electron donation from carbon to metal. The direction of electron transfer has been controversial, both theoretically and experimentally. Rigid-band models and tight-binding linear combination of atomic orbitals (LCAO) models suggest electron transfer from carbon to metal. This electron transfer is supported by the known chemical behavior of the compounds and similarities in the shapes of the valence bands. However, augmented plane wave (APW) and related calculations suggest electron donation in the opposite direction, and this is confirmed experimentally by x-ray photoelectron spectroscopy. These difficulties may be resolved by considering a narrowing of the *d*-band in forming the later transition-metal carbides (11). This results in greater occupation of the band, as deduced chemically, and simultaneous transfer of electrons from metal to nonmetal, as observed physically.

Diamondlike Carbides. Silicon and boron carbides form diamondlike carbides; beryllium carbide, having a high degree of hardness, can also be included. These materials have electrical resistivity in the range of semiconductors (qv), and the bonding is largely covalent. Diamond itself may be considered a carbide of carbon because of its chemical structure, although its conductivity is low.

Table 3 summarizes the properties of the so-called nonmetallic hard materials, including diamond and the diamondlike carbides B_4C, SiC, and Be_2C. Also included in this category are corundum, Al_2O_3, cubic boron nitride, BN, aluminum nitride, AlN, silicon nitride, Si_3N_4, and silicon boride, SiB (12).

Table 3. Physical Properties of Diamondlike Carbides and Nonmetallic Hard Materials

Compound	Molecular formula	Density, g/mL	Mp, °C	Microhardness[a]	Transverse rupture strength, N/mm²[b]	Compression strength, N/mm²[b]	Modulus of elasticity, N/mm²[b]	Heat conductivity, W/(cm·K)	Coefficient of thermal expansion, $\beta \times 10^{-6}$	Electrical resistivity, $\mu\Omega\cdot$cm
diamond	C	3.52	3,800 dec	7600	~300	~2,000	~900,000	1.14	0.9–1.18	10^{18}
boron carbide	B_4C	2.52	2,450	2940	500	1,800	450,000	0.27	6.0	10^{4}
silicon carbide	SiC	3.2	2,300 dec	2580	<400[c]	1,400	480,000	0.15	5.7	10^{3}
beryllium carbide	Be_2C	2.42	2,300	2690		740	350,000	0.21	7.4	10^{3}
alumina, sintered	Al_2O_3	3.9	2,050	2080	<700[c]	3,000	400,000	0.19	7.8	10^{18}
boron nitride, cubic	BN	3.45	2,730[d]	4700			600,000			10^{1}
aluminum nitride	AlN	3.26	2,250	1230			350,000			10^{13}
silicon nitride	Si_3N_4	3.44	1,900	1700	<750[c]		210,000	0.18	2.4	10^{1}
silicon boride	SiB	2.43	1,950	2300	~100		330,000		6.3	10^{5}

[a] See HARDNESS

[b] To convert N/mm² (MPa) to psi, multiply by 145

[c] Hot-pressed.

[d] Transition from cubic to hexagonal ~1650°C.

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CEMENTED CARBIDES

Cemented carbides belong to a class of hard, wear-resistant, refractory materials in which the hard carbides of Group 4–6 (IVB–VIB) metals are bound together or cemented by a soft and ductile metal binder, usually cobalt or nickel. Although the term cemented carbide is widely used in the United States, these materials are better known internationally as hard metals (see also REFRACTORIES; REFRACTORY COATINGS; REFRACTORY FIBERS).

Cemented carbides were first developed in Germany in the early 1920s. The first cemented carbide to be produced was tungsten carbide *[12070-12-1]*, WC, having a cobalt *[7440-48-4]*, Co, binder (1). A number of scientific and technological advances provided impetus to development (2): (*1*) discovery of the high hardness of cast WC; (*2*) production of fine particles of WC, by reaction of the elements or by carburizing with hydrocarbons (qv); (*3*) application of sintering technology to the carbides; (*4*) lowering of the high sintering temperature of pure carbides by the use of a liquid phase of eutectic alloys of the iron-group metals; and (*5*) discovery of a unique combination of properties of the WC–Co alloys, including high compressive strength, high elastic modulus, abrasion resistance, toughness, and thermal shock resistance.

Over the years, the basic WC–Co material has been modified to produce a variety of cemented carbides containing WC–TiC, WC–TiC–TaC, WC–TiC–(Ta,Nb)C, WC–Mo_2C–TiC, and other solid solutions which cover a wide range of applications including metal cutting, mining, construction, rock drilling, metal forming, structural components, and wear parts. Efforts to replace cobalt completely by nickel or iron in WC-based compositions have not been very successful, although partial replacement with nickel has been shown to offer benefits in certain applications (3).

Attempts to produce WC-free compositions for metal-cutting applications were made in the 1930s with the development of TaC–Ni, TiC–Mo_2C–Ni, and TiC–VC–Ni–Fe–Co alloys. But these alloys could not compete with the stronger WC–Co-based cutting tools. However, in the 1950s, an understanding of the role of molybdenum in improving the wettability of titanium carbide *[12070-08-5]*, TiC, to Ni binder brought the TiC–Mo–Ni alloys closer in performance to WC–Co-based tools in finish machining of steels. Further improvements in tool performance were obtained by additions of other carbides such as tantalum carbide *[12070-06-3]*, TaC, and niobium carbide *[12069-94-2]*, NbC, to the TiC–Mo–Ni alloys.

The first carbonitride alloys based on Ti(C,N)–Ni–Mo were introduced in 1970 followed by (Ti, Mo)(C,N)-based compositions having fine microstructures that provided a balance of wear resistance and toughness (4). Continued research on the titanium carbonitride alloys, often called TiC–TiN cermets, in the 1980s led to the development of complex cermets having a variety of additives such as molybdenum carbide(2:1) *[12069-89-5]*, Mo_2C, TaC, NbC, zirconium carbide *[12020-14-3]*, ZrC, hafnium carbide *[12069-85-1]*, HfC, WC, vanadium carbide *[12070-10-9]*, VC, chromium carbide (3:2) *[12012-35-0]*, Cr_3C_2, and aluminum, Al (5). Various mixes of these additives impart different combinations of wear resistance, thermal shock resistance, and toughness and allow tools to be tailored for a wide range of machining applications.

Manufacture

Cemented carbides are manufactured by a powder metallurgy process (see METALLURGY, POWDER) consisting of a sequence of carefully controlled steps designed to obtain a final product having specific properties, microstructure, and performance. As shown in Figure 1 the carbides or the carbide solid solution powders are prepared, powder blends are produced, the materials are compacted, presintered, and shaped, and the carbide subjected to sintering and postsintering operations. The sintered product may either be directly put to use or ground, polished, and coated.

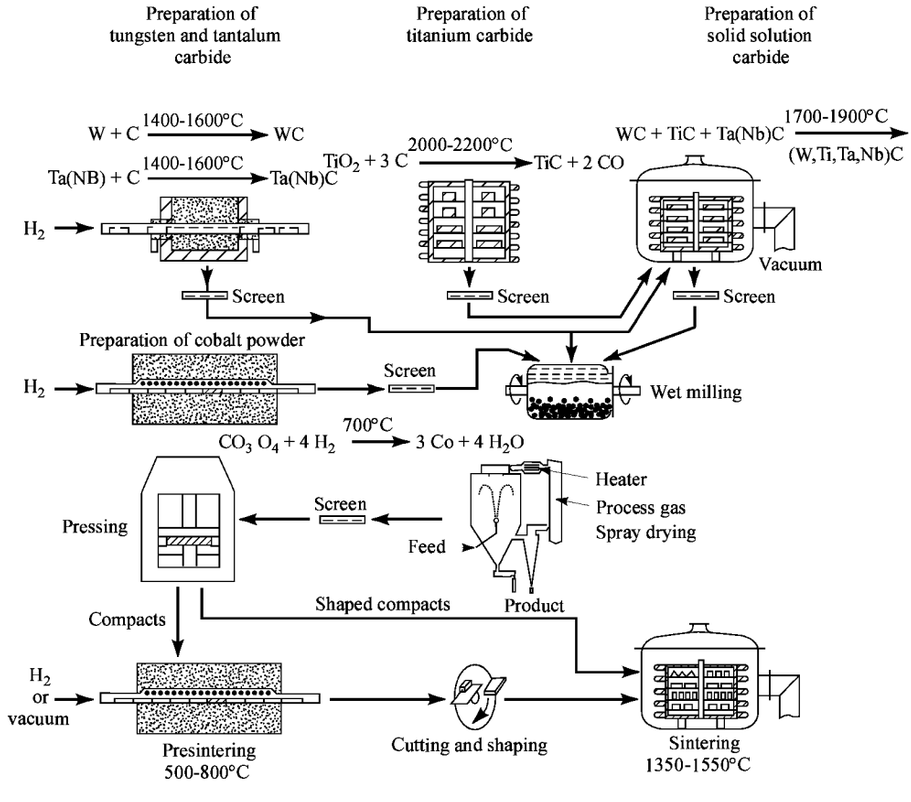

Fig. 1. Preparation of cemented carbides where cobalt serves as the binding metal.

The binder metal, cobalt or nickel, is obtained as very fine powder and is blended with the carbide powders in ball mills, vibratory mills, or attritors

using carbide balls. The mills are lined with carbide, low carbon steel, or stainless-steel sleeves. Intensive milling is necessary to break up the initial carbide crystallites and disperse the cobalt among the carbide particles to enhance wetting by cobalt during sintering. Milling is performed under an organic liquid such as alcohol, hexane, heptane, or acetone. In the milling process a solid lubricant such as paraffin wax or poly(ethylene glycol) is added to the powder blend to impart strength to the pressed or consolidated powder mix. After milling, the organic liquid is removed by drying. In a spray-drying process, commonly employed in the cemented carbide industry, a hot inert gas such as nitrogen impinges on a stream of carbide particles and produces free-flowing spherical powder aggregates.

The milled and dried grade powders are pressed to desired shapes in hydraulic or mechanical presses. Special shapes may require a presintering operation followed by machining or grinding to the final form. Cold isostatic pressing, followed by green forming, is also common in the manufacture of wear-resistant components and metal-forming tools. Rods and wires are formed by the extrusion process.

The pressed compacts are normally set on graphite trays and are initially heated ~500°C in a hydrogen atmosphere or vacuum for lubricant removal. Subsequently, the compacts are heated in vacuum to a final sintering temperature ranging from 1350 to 1550°C, depending on the amount of the metal binder and the microstructure desired. During final sintering the binder melts and draws the carbide particles together, shrinking the compact from 17 to 25% on a linear scale and producing a virtually pore-free, fully dense product.

In the 1970s, the cemented carbide industry adapted hot isostatic pressing (HIP) technology to remove any residual internal porosity, pits, or flaws from the sintered product (6). The HIP process involves reheating vacuum sintered material to 25 to 50°C less than the sintering temperature under a gaseous (argon) pressure of 100 to 150 MPa (14,500 to 21,750 psi). A more recent sintering technology, developed in the early 1980s called the sinter-HIP process (7), employs low pressure HIP, up to about 7 MPa (1015 psi), combined with vacuum sintering. The pressure is applied at the sintering temperature when the metallic binder is still molten, resulting in void-free products. After sintering, cemented carbide products that require shaping to meet surface finish, tolerance, or geometry requirements undergo grinding with metal-bonded diamond wheels or lapping with diamond-containing slurries.

Inhalation of extremely fine carbide, cobalt, and nickel powders should be avoided. Efficient exhaust devices, dust filters, and protective masks are essential when handling these powders.

Recycling of Scrap

Recycling of cemented carbide scrap is of growing importance. In one method, the scrap is heated to 1700–1800°C in a vacuum furnace to vaporize some of the cobalt and embrittle the material. After removal from the furnace the material is crushed and screened. In chemical recycling the cobalt is removed by leaching, leaving carbide particles intact. In the zinc reclaim process, commercialized in the late 1970s, the cleaned scrap is heated with molten zinc in an electric furnace under inert gas at ~800°C. The zinc reacts with the cobalt binder and the carbide pieces swell to more than twice their original volume. The zinc is distilled off in vacuum and reclaimed. The treated carbide pieces are pulverized and screened to produce a fine powder. The cobalt is still present in the particles and there is no change in grain size from the original sintered scrap. The coldstream reclaim method employs a high velocity airstream to accelerate cemented carbide particles against a target surface having sufficient energy to cause the particles to fracture. The coldstream process, so called because the air cools as it expands from the nozzles, is employed in combination with the zinc reclaim process.

Separate classifications exist for metal-cutting applications and wear parts (8). Classifications that are generally accepted by producers and users are available (9,10).

Tool Wear Mechanisms

The performance of a tool material in a given application is dictated by its response to conditions at the tool tip. High temperatures and stresses can cause blunting from the plastic deformation of the tool tip, whereas high stresses alone may lead to catastrophic fracture. In addition to plastic deformation and fracture, the service life of cutting tools is determined by a number of wear processes, some of which are shown in Figure 2.

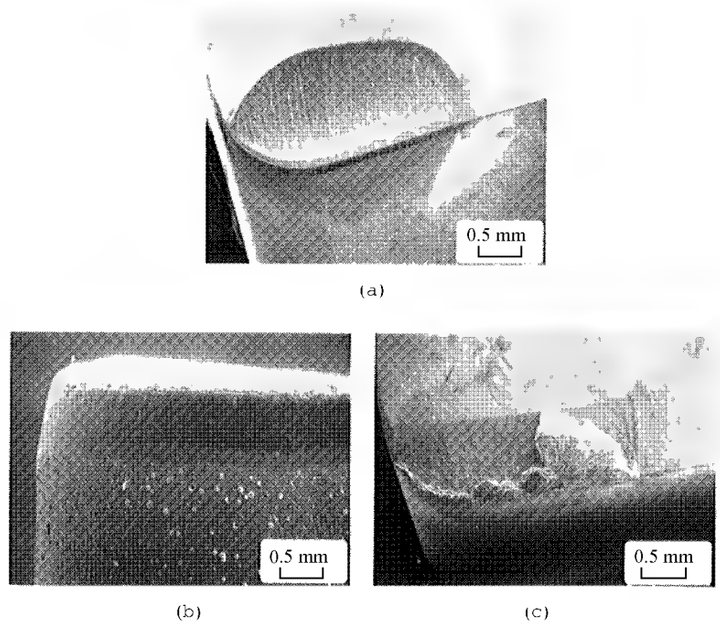

Fig. 2. Tool wear mechanisms. (**a**) Crater wear on a cemented carbide tool produced during machining plain carbon steel. (**b**) Abrasive wear on the flank face of a cemented carbide tool produced during machining gray cast iron. (**c**) Built-up edge produced during low speed machining of a nickel-based alloy.

Crater Wear. Crater wear (Fig. 2**a**) is caused by a chemical interaction between the rake face of a metal-cutting insert and the hot metal chip flowing over the tool. This interaction may involve diffusion or dissolution of the tool material into the chip.

Flank Wear. Flank or abrasive wear (Fig. 2**b**) is often observed on the flank face of an insert or at the working end of wear parts or mining tools and is related to the hardness of the tool material. Harder tool materials provide greater flank and abrasive wear resistance.

Built-up Edge. At relatively low speeds in metal-cutting operations, the tool tip does not get hot enough for crater wear to be significant. Under these conditions the metal may, however, become welded to the tool tip as built-up edge (Fig. 2**c**).

Depth-of-Cut Notching. Depth-of-cut notching (DOCN) is a localized wear process common when machining materials such as austenitic stainless steels or high temperature alloys. Notching is attributed to the chemical reaction of the tool material and the atmosphere, or to abrasion by the hard, sawtooth outer edge of the chip. DOCN may lead to tool fracture.

Thermal Fatigue. Cemented carbide tools sometimes exhibit a series of cracks perpendicular to the tool edge when applied in interrupted cutting conditions such as milling. These thermal cracks are caused by the alternating expansion and contraction of the tool surface as it heats while cutting

and then cools outside the cut. With prolonged intermittent cutting, lateral cracks may appear parallel to the cutting edge. The thermal and lateral cracks may join together and cause small fragments of tool material to break away.

Evaluation of Properties

In addition to chemical analysis a number of physical and mechanical properties are employed to determine cemented carbide quality. Standard test methods employed by the industry for abrasive wear resistance, apparent grain size, apparent porosity, coercive force, compressive strength, density, fracture toughness, hardness, linear thermal expansion, magnetic permeability, microstructure, Poisson's ratio, transverse rupture strength, and Young's modulus are set forth by ASTM ANSI and the ISO.

Among the physical properties, cemented carbide density is very sensitive to composition and porosity of the sample and is widely used as a quality control test. Magnetic properties most often measured are magnetic saturation and coercive force. Magnetic saturation provides an accurate measure of the carbon content in the cemented carbide alloy and is also used as a quality control test. The carbon content must be controlled within narrow limits to prevent the formation of a brittle eta-phase, of composition Co_3W_3C or Co W C, at low carbon levels, or free graphite where carbon levels are high. Coercive force may vary considerably as sintering temperature increases and indicates the structural changes that take place during sintering. For a given cobalt and carbon content, the coercive force provides a measure of the size and distribution of the carbide phase in the microstructure.

The properties and performance of cemented carbide tools depend not only on the type and amount of carbide but also on carbide grain size and the amount of binder metal. Information on porosity, grain size and distribution of WC, solid solution cubic carbides, and the metallic binder phase is obtained from metallographically polished samples. Optical microscopy and scanning and transmission electron microscopy are employed for microstructural evaluation. Typical microstructures of cemented carbides are shown in Figure 3.

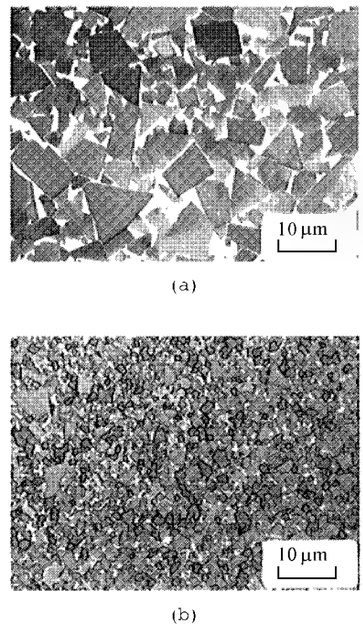

Fig. 3. Microstructures of cemented carbides. (**a**) 94% WC–6% Co alloy, coarse grain. (**b**) 85% WC–9% (Ta,Ti,Nb)C–6% Co alloy, medium grain size. The gray angular particles are WC and the dark gray rounded particles are solid solution carbides. The white areas are cobalt binder.

Hardness (qv), which determines the resistance of a material to abrasion and deformation, is affected not only by composition but also by porosity and microstructure. Higher cobalt content and larger carbide grain size reduce hardness and abrasion resistance but increase the toughness of cemented carbides. The trade-off of abrasion resistance and toughness enables the cemented carbide manufacturer to tailor these materials to a wide variety of metal-cutting and nonmetal-cutting applications.

Hardness is measured by the Rockwell A-scale diamond cone indentation test (HRA) or by the Vickers diamond pyramid indentation test (HV). Although the Rockwell scale has been used for decades in the carbide industry as a measure of hardness, a true indication of the resistance of the tool to deformation in metal-cutting operations can be obtained only by measuring hardness at elevated temperatures. The hardness of cemented carbides decreases monotonically with increasing temperatures.

Cemented carbides possess high compressive strength but low ductility at room temperature, but at temperatures associated with metal-cutting these materials exhibit a small but finite amount of ductility. Measurement of yield strength is therefore more appropriate at higher temperatures. Like hardness, the compressive yield strength of cemented carbide decreases monotonically with increasing temperatures.

The most common method of determining the fracture strength of cemented carbides is the transverse rupture strength (TRS) test. A disadvantage of this test is the large scatter in the experimental data resulting from surface defects in the test specimens. Nevertheless, TRS is an excellent quality control test and it is particularly useful for large carbide components. A better measure of the intrinsic strength of the cemented carbide is the fracture toughness parameter, K_{Ic}, which indicates the resistance of a material to fracture in the presence of a sharp crack (11). The fracture toughness of carbide materials increases with cobalt content and carbide grain size but decreases with additions of cubic carbides.

Metal-Cutting Applications

Tools and Toolholding. Early carbide metal-cutting tools consisted of carbide blanks brazed to steel holders. Indexable inserts were introduced in the 1950s. In this configuration the so-called throwaway carbide insert is secured in the holder pocket by a clamp or some other holding device instead of a braze. When a cutting edge wears, a fresh edge is rotated or indexed into place. The main advantages of indexable inserts are ease of replacement, consistent positioning of the cutting edge relative to the workpiece, elimination of regrinding, and the ability to coat the inserts with the chemical vapor deposition (CVD) and the physical vapor deposition (PVD) processes. Indexable inserts also feature chipbreaker grooves, which not only control chip formation but also lower cutting forces. The edges of both brazed tools and indexable inserts are often modified, slightly rounded (honed) or chamfered, to prevent chipping and premature failure of a too sharp and therefore weak cutting edge.

Compositions. For machining purposes, alloys having 3 to 12 wt % Co and carbide grain sizes from 0.5 to >5 μm are commonly used. The straight WC–Co alloys have excellent resistance to simple abrasive wear and are widely used in machining materials that produce short chips, eg, gray cast-iron, nonferrous alloys, high temperature alloys, etc. WC–Co alloys having submicrometer carbide grain sizes have been developed for applications requiring more toughness or tool edge strength. Such applications include indexable metal-cutting inserts and a wide variety of solid carbide drilling and milling tools. Grain refinement in these alloys is obtained by small (0.25–3.0 wt %) additions of TaC, NbC, VC, or Cr_3C_2 during carburization of tungsten

or later in the powder blend.

Straight WC–Co tools are not suitable for machining steels that produce long chips because straight grades undergo crater wear from diffusion of WC into the steel chip surface. However, solid solutions of WC–TiC, WC–TiC–TaC, etc, resist this type of chemical attack. In addition, tantalum carbide can improve thermal-shock resistance. Steel cutting compositions thus typically contain WC–TiC–(Ta,Nb)C–Co. Tantalum carbide is often added as (Ta,Nb)C because the chemical similarity between TaC and NbC makes their separation expensive.

Coated Carbide Tools. Chemical vapor deposited (CVD) TiC coatings were used in the early 1970s to combat wear on steel watch parts and cases. When applied to cutting tools, the relatively thin (~5 μm) TiC coatings extend tool life in steel and cast-iron machining by a factor of two to three by suppressing the crater wear and flank wear (12). Hard coatings also reduce frictional forces at the chip tool interface, which in turn reduce the heat generated in the tool resulting in lower tool tip temperatures. In 1991, coated carbides accounted for nearly 65% of all indexable metal-cutting inserts used in the United States.

In the CVD coating process, the tools are heated in a sealed reactor with gaseous hydrogen at atmospheric or lower pressure; volatile compounds are added to the hydrogen to supply the metallic and nonmetallic constituents of the coating. For example, TiC coatings are produced by reaction of $TiCl_4$ vapors with methane (CH_4) and hydrogen (H_2) at 900 to 1100°C. The reaction is

$$TiCl_4(g) + CH_4(g) + H_2(g) \rightarrow TiC(s) + 4\,HCl(g) + H_2(g)$$

During the initial stage of the TiC deposition, a secondary reaction often occurs in which carbon is taken from the cemented carbide substrate. The resulting surface decarburization leads to the formation of a brittle η-phase and associated microporosity at the coating substrate interface. The η-phase in turn can produce premature tool failure resulting from excessive chipping and reduced edge strength (13). However, improvements in CVD coating technology have resulted in coatings with greater thickness uniformity, more adherence, and more consistent morphology and microstructure having minimum interfacial η-phase and associated porosity (14).

CVD coatings themselves have also evolved from single-layer TiC coatings having narrow application ranges to multilayer hard coatings comprising various combinations of TiC, titanium carbide nitride *[12347-09-0]*, TiCN, titanium nitride *[25583-20-4]*, TiN, alumina, Al_2O_3, and occasionally hafnium nitride *[25817-87-2]*, HfN (Fig. 4**a** and 4**b**). A trend also exists toward the use of multiple alternating coating layers (Fig. 4**c**), which are believed to produce finer grain sizes, minimize chipping, and extend the range of application of the coated tools (15).

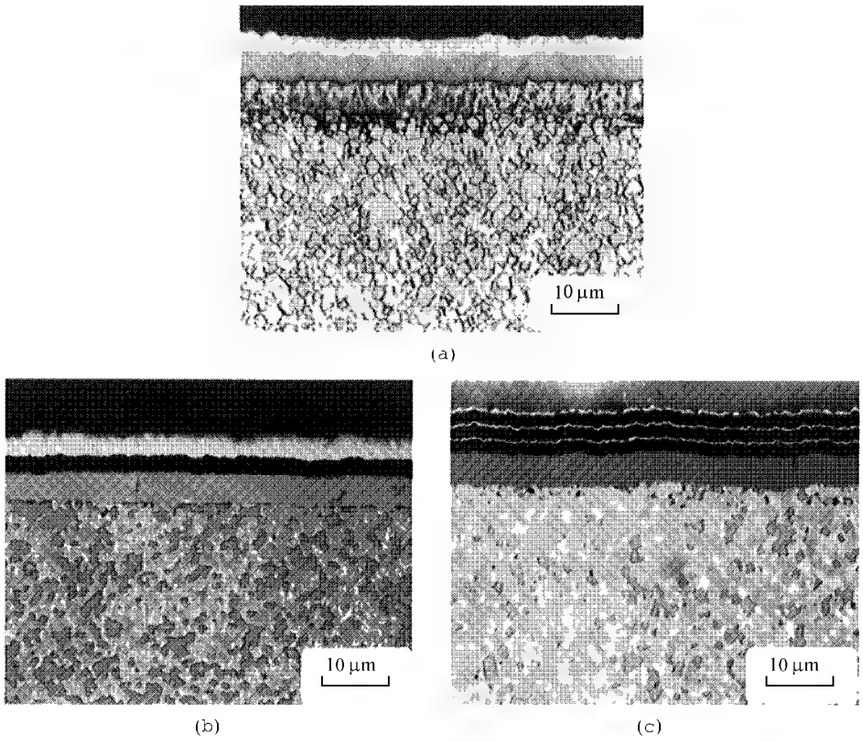

Fig. 4. Multilayer coatings on cemented carbide substrates. (**a**) 73% WC–19%(Ta,Ti,Nb)C–8%Co alloy with a TiC–TiCN–TiN coating of about 10 μm total thickness. (**b**) 85%WC–9%(Ti,Ta,Nb)C–6%Co with a TiC–Al_2O_3–TiN coating about 9 μm thick. (**c**) 86%WC–8%(Ta,Ti,Nb)C–6%Co with TiCN coating supporting multiple alternating coating layers of Al_2O_3 and TiN.

The high temperatures employed during CVD coating generally ensure good bonding between the substrate and the coating. However, the thermal expansion mismatch between the substrate and the coating can cause stresses that adversely affect coating adhesion. In certain cases coating stresses may be relieved by cracks that form in the coating. Because the thermal expansion coefficients of the coating materials (TiC, TiCN, TiN, and Al_2O_3) are higher than those of the WC–Co-based substrates, CVD coatings are in residual tension at room temperature. Residual tensile stresses are most severe at tool corners. To minimize stress, CVD-coated tools are honed before coating.

A breakthrough in coated carbide cutting tools occurred in the late 1970s when a peripherally cobalt-enriched substrate was developed for a TiC–TiCN–TiN-coated tool (Fig. 5). The combination provided superior edge strength while maintaining the edge and crater wear resistance of the coating layers (16). This development permitted users to make heavy interrupted machining cuts such as those encountered in scaled forgings and castings at lower speeds. Further refinements to the cobalt-enrichment concept have expanded the application range of this type of tool to higher speeds (17,18).

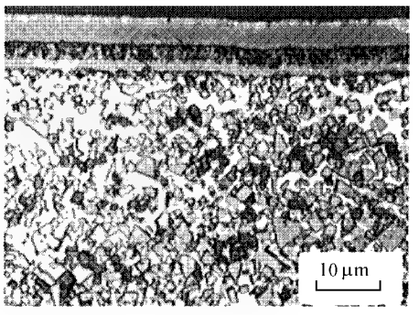

Fig. 5. Microstructure of a cemented carbide alloy, 86% WC–8% (Ti,Ta,Nb)C–6% Co, with a cobalt-enriched periphery and a TiC–TiCN–TiN coating.

In the 1980s physical vapor deposition (PVD) emerged as a commercially viable process for applying hard TiN coatings onto cemented carbide tools. A number of factors make PVD process attractive for use with cemented carbide tools: (*1*) lower deposition temperature (<700°C) prevents η-phase formation and produces finer grain sizes in the coating layer; (*2*) PVD coatings are usually crack-free; (*3*) depending on the deposition technique, compressive residual stresses, which are beneficial in resisting crack propagation, may be introduced in the coating (19); (*4*) PVD coating preserves the transverse rupture strength of the carbide substrate, whereas the CVD process generally reduces the TRS by as much as 30% (20); (*5*) PVD coatings can be applied uniformly over sharp cutting edges (Fig. 6). This is desirable because it leads to lower cutting forces, reduced tool tip temperatures, and finer workpiece finishes. PVD coated tools are thus successfully employed in operations where sharp edges are most beneficial, including milling, turning, boring, threading, and grooving. Newer compositions are rapidly becoming commercially available. These include TiCN, titanium aluminum nitride which ranges in composition from Ti_2AlN *[60317-94-4]* to TiAlN, chromium carbide *[12011-60-8]*, CrC, and chromium nitride *[24094-93-7]*, CrN.

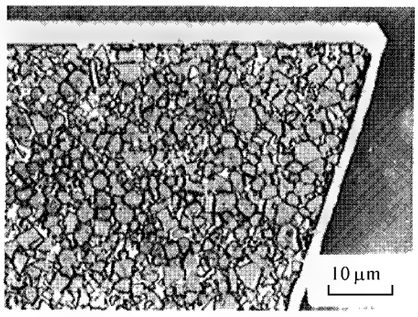

Fig. 6. An example of PVD TiN coating on a sharp cemented carbide tool.

Nonmetal-Cutting Applications

In the early 1990s almost half of the total production of cemented carbides was used for nonmetal-cutting applications such as mining, oil and gas drilling, transportation and construction, metalforming, structural and fluid-handling components, and forestry tools. The majority of compositions used in these applications comprised straight WC–Co grades. In general, cobalt contents vary from 5 to 30 wt % and WC grain sizes range from <1 to <8 μm and sometimes to 30 μm. Extensive discussion of hard metals employed in nonmachining applications is available (21–24).

Metal-forming applications include drawing dies, rolls for hot and cold forming of strips and bars, cold heading dies, forward and back extrusion punches, swaging hammers and mandrels, and can body punches and dies. Applications requiring high impact strength employ grades with 11 to 25 wt % Co. When wear resistance is of paramount importance, grades having lower cobalt content and finer grain size are suitable choices. When gall resistance, ie, resistance to metal pickup on the tool, is needed, alloy carbides such as (W,Ti)C and (Ta,Nb)C are used. Corrosion resistance applications typically employ grades having finer WC grain sizes and lower cobalt contents or combinations of nickel, cobalt, and chromium.

The impetus for the synthesis of WC and subsequent development of cemented carbides came from the wire drawing industry where the hard metals are still used. The most commonly used grade is WC-6 wt % Co with medium grain size (1–2 μm). Compositions having higher cobalt content are used in drawing tubes, rods, and bars.

Alloys having 15 to 30 wt % Co and very coarse WC grain sizes (up to 20 μm) have replaced steel rolls in the production of hot-rolled steel rods. Carbide rolls are also well suited for the cold reduction and finishing of strip products in Sendzimir mills where rigidity and dimensional stability are particularly important. The compositions used in these applications have a 5.5 wt % Co and medium WC grain size (1–2 μm).

The high abrasion resistance and edge strength of carbides make them ideal for use as slitter knives for trimming steel cans and stainless and carbon steel strips, cutting abrasive materials in the paper (qv), cellophane and plastic industries, and for slitting magnetic tapes for audio, video, and computer applications. Carbides having submicrometer grain sizes and 6–10 wt % Co offer sharp cutting edges, good surface finish, and high edge strength in these applications.

Cold-forming equipment such as extrusion or heading punches and dies are made from cemented carbides to produce a variety of parts such as wrist pins, spark plug shells, bearing retainer cups, and propeller shaft ends. Generally, WC-12 wt % Co alloy is used for back extrusion punches and a WC-16 wt % Co grade is recommended for extrusion dies. Submicrometer carbides may also be used for punches. In cold-heading applications involving the manufacture of nuts, bolts, and screws the dies have to withstand considerable stress and repeated impacts and must therefore possess good fatigue strength. Alloys with 20–30 wt % Co are required.

The high elastic modulus, compressive strength, and wear resistance of cemented carbides make them ideal candidates for use in boring bars, long shafts, and plungers, where reduction in deflection, chatter, and vibration are concerns. Metal, ceramic, and carbide powder-compacting dies and punches are generally made of 6 wt % and 11 wt % Co alloys, respectively. Another application area for carbides is the synthetic diamond industry where carbides are used for dies and pistons (see CARBON).

The rigidity, hardness, and dimensional stability of cemented carbides, coupled with their resistance to abrasion, corrosion, and extreme temperatures, provide superior performance in fluid-handling components such as seal rings, bearings, valve stems and seats, and nozzles. In the transportation and construction industry, steel tools having cemented carbide cutting tips are used for road planing, soil stabilization, asphalt reclamation, vertical and horizontal drilling, trenching, dredging, tunnel boring, forestry, and for snowplow blades, tire studs, and street sweeper skids.

Cemented carbides play a crucial role in the recovery of metallic ores and nonmetals by underground or open-pit mining practices, recovery of minerals such as coal (qv), potash, and trona, and drilling for oil and gas. The methods of excavation can be broadly classified into three types: rotary

drilling, roto-percussive drilling, and flat-seam underground mining. In the oil and gas drilling industry tungsten carbide buttons, having 10–15 wt % Co, are used in steel drill bodies for deep penetration of metamorphic and crystalline rocks.

Cemented tungsten carbides also find use as a support for polycrystalline diamond (PCD) cutting tips, or as a matrix alloy with cobalt, nickel, copper, and iron, in which diamond particles are embedded. These tools are employed in a variety of industries including mineral exploration and development; oil and gas exploration and production; and concrete, asphalt, and dimension stone cutting.

Economic Aspects

Cemented carbide inserts and tools for metal-cutting and metal-working have traditionally accounted for the largest percentage of carbide industry sales. However, carbide tool consumption in nonmetal-working fields, notably in the construction and transportation industries, has grown rapidly. On the other hand, the demand for primary materials has been somewhat reduced by use of recycled cemented carbide scrap.

There are more than 200 cemented carbide producers in the world. A majority of hard metal production can be attributed to Cerametal Sarl, GTE Valenite Corporation, Kennametal Inc., Krupp Widia GmbH, Mitsubishi Metal Corporation, Plansee Tizit GmbH, Rogers Tool Works Inc., AB Sandvik Coromant, Sumitomo Electric Industries Ltd., Teledyne Firth Stirling, Toshiba Tungaloy Co. Ltd., and Zhuzhou Cemented Carbide Industry Company. Many of the smaller producers have narrow manufacturing capabilities and a limited range of product offerings.

Developments in materials, coatings, and insert geometries have claimed an increasing share of research and development budgets in the cemented carbide industry. An important economic benefit of these effects has been an increase in tool performance. Continuing developments in computer-numerically-controlled machining systems have placed a heavy emphasis on tool reliability and consistency, which in turn puts pressure on the industry to invest increasing amounts of capital in developing new materials and processes.

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INDUSTRIAL HARD CARBIDES

The four most important carbides for the production of hard metals are tungsten carbide *[12070-12-1]*, WC, titanium carbide *[12070-08-5]*, TiC, tantalum carbide *[12070-06-3]*, TaC, and niobium carbide *[12069-94-2]*, NbC. The binary and ternary solid solutions of these carbides such as WC–TiC and WC–TiC–TaC (NbC) are also of great importance. Chromium carbide (3:2) *[12012-35-0]*, Cr_3C_2, molybdenum carbide *[12011-97-1]*, MoC, and molybdenum carbide (2:1) *[12069-89-5]*, Mo_2C, vanadium carbide *[12070-10-9]*, VC, hafnium carbide *[12069-85-1]*, HfC, and zirconium carbide *[12020-14-3]*, ZrC, have minor significance. Carbides and their solid solutions are generally combined with cobalt and used in the form of cemented carbides. The carbides of the actinides, Th, U, Pu, and Np, have gained importance in reactor technology as nuclear fuels (see NUCLEAR REACTORS).

Preparation

In general, the carbides of metals of Groups 4–6 (IVB–VIB) are prepared by reaction of elementary carbon or hydrocarbons and metals and metal compounds at high temperatures. The process may be carried out in the presence of a protective gas, under vacuum, or in the presence of an auxiliary metal (menstruum).

Carburization By Fusion. This method is used for the preparation of tungsten carbide for the mineral industry, ie, for coarse-grained powder or castings for welding (qv) onto oil drills and wear-resistant parts.

$$3\,W + 2\,C \xrightarrow{2800^\circ C} W_2C{-}WC$$

The product, W_2C–WC, is a eutectic cast carbide.

Carburization by Thermal Diffusion. Carburization of chemically processed metal or metal-compound powders is carried out through solid-state, thermal diffusion processes, either in protective gas or vacuum. Carbide solid solutions are prepared by the same methods. Most carbides are made by these processes, using loose or compacted mixtures of carbon and metal or metal-oxide powders. Halides of Group 5 (VB) metals recovered from ores by chlorination are similarly carburized.

$$W + C \xrightarrow{1400-1600^\circ C} WC \tag{1}$$

$$Ta(H) + C \xrightarrow[H_2,\ \text{vacuum}]{1400-1500^\circ C} TaC + (H)$$

$$W + CH_4 \xrightarrow[H_2]{1400-1600^\circ C} WC + 2\,H_2$$

$$WO_3 + 4\,C \xrightarrow[H_2,\ CO]{1400-1600^\circ C} WC + 3\,CO \tag{2}$$

$$TiO_2 + 3\,C \xrightarrow[H_2,\ CO,\ \text{vacuum}]{1800-2000^\circ C} TiC + 2\,CO$$

$$Nb_2O_5 + 6\,C + CH_4 \xrightarrow[H_2]{1400-1700^\circ C} 2\,NbC + 5\,CO + 2\,H_2$$

Carburization by Menstruum Process. The P. M. McKenna method of carburization (1) involves the use of mineral concentrates such as wolframite *[1332-08-7]*, $Fe(Mn)WO_4$, and microlite *[12173-96-5]*, $Ca_2Ta_2O_7$, ferroalloys such as iron tungstide, FeW, or high purity scrap metals in a high temperature melt of auxiliary (menstruum) metal or metals, with carbon. Upon cooling, carbide crystals are dispersed throughout the metallic mass. The mass is then crushed and the carbide crystals isolated by dissolving the menstruum alloy in mineral acids. Further purification by elutriation follows.

$$Fe(Mn)\,WO_4 + 5\,C + Fe \xrightarrow{2300-2600^\circ C} WC + Fe(Mn) + Fe + 4\,CO + C$$

$$FeW + 2\,C \xrightarrow{2300-2600^\circ C} WC + Fe + C$$

$$TiO_2 + Fe + 4\,C \xrightarrow{2300-2600^\circ C} TiC + Fe + 2\,CO + C$$

$$FeW + Ti + Fe + 2\,C \xrightarrow{2300-2600^\circ C} (W,Ti)\,C + 2\,Fe + C$$

$$Ca_2Ta_2O_7 + Fe + 13\,C \xrightarrow{2300-2600^\circ C} 2\,TaC + Fe + 7\,CO + 2\,CaC_2 + C$$

Carburization by Thermochemical Reaction. Carburization of tungsten contained in tungsten mineral concentrates is accomplished by means of a simultaneous aluminothermic reduction and carburization (2,3). The reaction produces, upon cooling, a metallic mass in which tungsten carbide crystals are dispersed in a menstruum alloy. After crushing, WC crystals in the mass are isolated by dissolving the menstruum either in acidic ferric chloride solutions or mineral acids. The process has, since the 1960s, become an important source of primary WC for the manufacture of cemented hard carbides and other metallurgical products.

$$6\,Fe(Mn)\,WO_4 + 22\,Al + 3\,CaC_2 + 3\,Fe_3O_4 \xrightarrow{2500-3000^\circ C} 6\,WC + 6\,Fe(Mn) + 9\,Fe + 3\,CaO + 11\,Al_2O_3$$

Titanium carbide may be prepared by a thermochemical reaction between finely divided carbon and titanium metal powder. The reaction proceeds exothermically.

$$Ti + C \xrightarrow{1700-2200^\circ C} TiC$$

Reduction. Reduction of halides using hydrogen–hydrocarbon mixtures is sometimes done in the presence of a graphite carrier or using metals possessing high melting points, ie, the van Arkel gas deposition method (4). If a plasma gun is employed, finely powdered (<1 μm) carbides are obtained

(5) (see PLASMA TECHNOLOGY). Chemical vapor deposition (CVD) is used for TiC, TiN, and Ti(C, N) coatings on cemented carbide inserts.

$$2\,TaCl_5 + C_2H_2 + 4\,H_2 \xrightarrow[\text{graphite}]{1300-1500^\circ C} 2\,TaC + 10\,HCl$$

$$HfCl_4 + CH_4 \xrightarrow[H_2,\ W\ \text{wire}]{2400-2800^\circ C} HfC + 4\,HCl$$

$$NbCl_5 + \frac{5}{2}H_2 \xrightarrow{500-600^\circ C} Nb + 5\,HCl \quad Nb + C \xrightarrow[CH_4,\ CO,\ H_2]{1300-1500^\circ C} NbC$$

Tungsten Carbide

Traditionally, tungsten ore is chemically processed to ammonium paratungstate *[1311-93-9]*, $(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$, and tungsten oxides, W_xO_y. These compounds are then hydrogen-reduced to tungsten *[7440-33-7]* metal powder (see TUNGSTEN AND TUNGSTEN ALLOYS; TUNGSTEN COMPOUNDS). The fine tungsten powders are blended with carbon and heated in a hydrogen atmosphere between 1400 and 1500°C to produce tungsten carbide particles having sizes varying from 0.5 to 30 μm. Each particle is composed of numerous tungsten carbide crystals. Small amounts of vanadium, chromium, or tantalum are sometimes added to tungsten and carbon powders before carburization to produce very fine (<1 μm) WC powders.

The characteristics of WC, especially grain size, are determined by purity, particle shape and grain size of the starting material, and the conditions employed for reduction and carburization. The course of the reaction $WO_3 \rightarrow W \rightarrow WC$ is dependent on temperature, gas flow rates, water-vapor concentration in the gas, and the depth of the powder bed. All these factors affect the coarsening of the grain.

Selection of suitable tungsten-containing raw materials and modification of the reduction and carburization conditions permit the preparation of the WC powder in various grain sizes. The following examples are illustrative: (*1*) very pure tungstic acid of fine (<0.1 μm) grain size is reduced in dry hydrogen at approximately 800°C, and the fine (<0.5 μm) tungsten powder obtained gives very fine (<1 μm) grained WC on carburization at 1350–1400°C; (*2*) calcined coarse (<2 μm) WO_3, after reduction with hydrogen in the presence of water vapor at 900–950°C, provides tungsten powder (<6 μm) from which coarse (<10 μm) crystalline WC powder can be prepared by carburization at 1600°C.

The WC leaving the furnace is light gray with a bluish tinge. It is generally caked and must be broken up, milled, and screened before use. It should contain about 6.1–6.25 wt % total C, of which 0.03–0.15 wt % is in the free, unbound state. The theoretical C-content is 6.13 wt %. Annual world production of tungsten monocarbide is 15,000–18,000 metric tons.

The thermochemical McKenna process proceeds from tungsten–mineral concentrates to produce tungsten carbide crystals and crystal fragments ranging in size from about 840 through 44 μm. Macrocrystalline WC, as grown in a menstruum alloy, forms well-developed, angular crystals having a triangular habit. The crystals always contain a perfectly stoichiometric bound-carbon content and are monocrystalline. Both in initially coarse form, and after size-reduction by milling, macrocrystalline WC has comparatively low specific surface and is entirely free of W_2C. Powders are prepared over a wide range of particle sizes, from granular screen-sized ranges to micron-sized powders.

Both macrocrystalline WC and the fused WC–W_2C eutectic (Fig. 1) are important in the manufacture of diamond drill bits used in the mining, oil and gas, and construction industries, and in hardfacing rods and electrodes. The properties of WC are listed in Table 1.

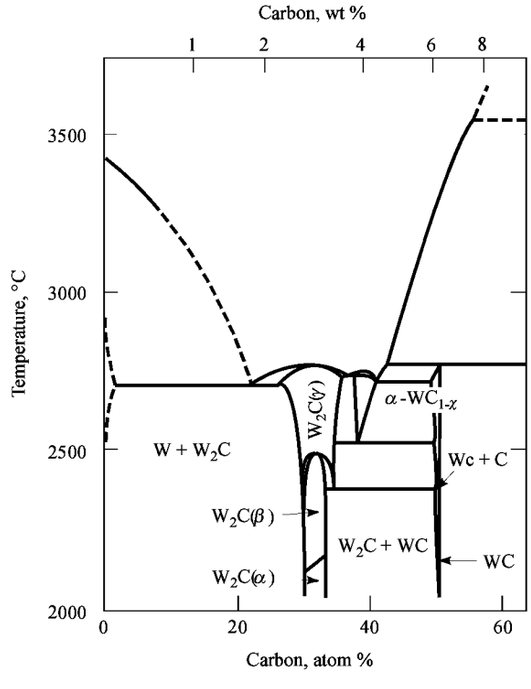

Fig. 1. Phase diagram for W–C.

Table 1. Physical Properties of Primary Carbides

Property	WC	TiC	TaC	NbC
mol wt	195.87	59.91	192.96	104.92
carbon, wt %	6.13	20.05	6.23	11.45
crystal structure	hex, Bh	fcc, B1	fcc, B1	fcc, B1
lattice constants, nm	*a* 0.29065 *c* 0.28366	0.43305	0.4454	0.4470
density, g cm^3	15.7	4.93	14.48	7.78
mp, °C	2720	2940	3825	3613
microhardness, kg mm^2	1200–2500	3000	1800	2000
modulus of elasticity, N mm^{2a}	696,000	451,000	285,000	338,000

transverse rupture strength, N mm^{2}[a]	550–600	240–400	350–450	300–400
coefficient of thermal expansion, K^{-1}	a 5.2 × 10^{-6} c 7.3 × 10^{-6}	7.74 × 10^{-6}	6.29 × 10^{-6}	6.65 × 10^{-6}
thermal conductivity, W (m·K)	121	21	22	14
heat of formation, $\Delta H_{f,298}$, kJ mol^{-1}[b]	−40.2	−183.4	−146.5	−140.7
specific heat, J (mol·K)[b]	39.8	47.7	36.4	36.8
electrical resistivity, $\mu\Omega$·cm	19	68	25	35
superconducting temperature, <K	1.28	1.15	9.7	11.1
Hall constant, cm^{3} (A·s)$^{-1}$	−21.8 × 10^{-4}	−15.0 × 10^{-4}	−1.1 × 10^{-4}	−1.3 × 10^{-4}
magnetic susceptibility	−10	−6.7	−9.3	−15.3

[a] To convert N mm^{-2} (MPa) to psi, multiply by 145.

[b] To convert J to cal, divide by 4.184.

Titanium Carbide

Annual world production of titanium carbide is 1200–1500 metric tons. On an industrial scale, it is produced most often through the reaction of TiO_2 with carbon black (see TITANIUM AND TITANIUM ALLOYS; TITANIUM COMPOUNDS).

In industrial production of titanium carbide, pure (99.8%, with minor impurities of Si, Fe, S, P, and alkalies) titanium oxide *[13463-67-7]*, TiO_2, in the dry or wet state is mixed in 68.5:31.5 ratio with carbon black or finely milled low ash graphite. The dry mixture is pressed into blocks that are heated in a horizontal or vertical carbon-tube furnace at 1900–2300°C; hydrogen that is free of oxygen and nitrogen serves as protective gas. In the vertical push-type furnaces, the liberated CO itself provides protection.

Titanium carbide is generally obtained in the form of gray, well-sintered lumps that are broken up in jaw-crushers and fine-milled in ball mills. Technical-grade TiC contains 0.5–1.5 wt% graphite, in addition to 0.5–1 wt% oxygen and nitrogen and 0.1 wt% impurities, such as Fe, Si, S, and P. The oxygen and nitrogen content may be reduced to 0.1–0.3 wt% by heating the impure carbides under high vacuum for several hours at 2000–2500°C, or less expensively, by formation of solid WC solutions, with or without the use of Mo_2C or Cr_3C_2.

Titanium carbide is also prepared by the menstruum method (6), starting with ferrotitanium, TiO_2, or titanium *[7440-32-6]*, Ti, metal. Comparatively low levels of oxygen and nitrogen are achieved because of strong outgassing under high temperature liquid menstruum alloy. Menstruum-made TiC strongly reflects the cubic crystal form, initially ranging in size from about 149 down through 44 µm. Bound carbon in the unmilled crystals is comparatively high, about 19.7 wt%. Properties of titanium carbide are listed in Table 1; the Ti–C phase diagram is shown in Figure 2.

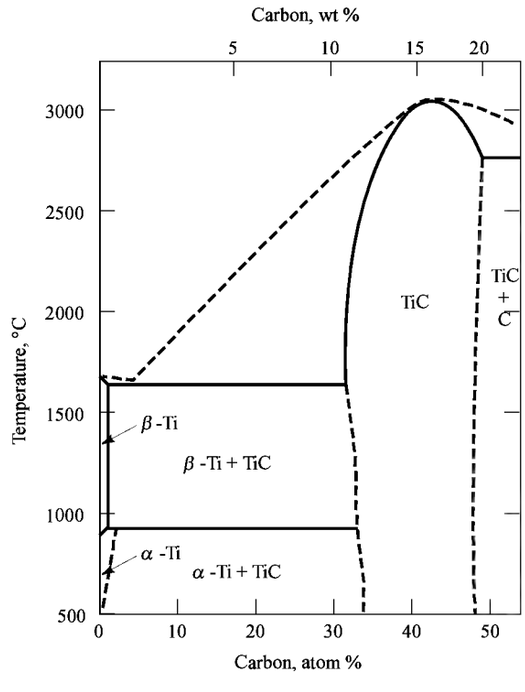

Fig. 2. Phase diagram for Ti–C.

Hardness and solubility for other carbides make TiC an important component of sintered cemented carbides. Although the addition of TiC or $WTiC_2$ to WC–Co alloys imparts crater wear resistance, it also reduces the transverse rupture strength and fracture toughness of these alloys. Therefore, the amount of TiC or $WTiC_2$ added to WC–Co alloys for steel machining is kept to a minimum, typically no greater than 10 wt%. The TiC-based cermets, on the other hand, may contain 30–85 wt% TiC.

Next to Cr_3C_2, TiC is the principal component for heat and oxidation-resistant cemented carbides. TiC-based boats, containing aluminum nitride, AlN, boron nitride, BN, and titanium boride, TiB_2, have been found satisfactory for the evaporation of metals (see BORON COMPOUNDS, REFRACTORY BORON COMPOUNDS; NITRIDES).

Tantalum Carbide

On an industrial scale, TaC is prepared from tantalum *[7440-25-7]*, Ta, metal or tantalum hydride *[12026-09-4]*, Ta_2H, powder, tantalum pentoxide *[1314-61-0]*, Ta_2O_5, high purity scrap obtained in the preparation of ductile Ta, or from ferrotantalum–niobium. The chemical and metallurgical industry uses tantalites, niobites, Ta–Nb-containing tin slags, and sometimes the ores microlite and pyrochlore *[12174-36-6]* for the preparation of tantalum (see TANTALUM AND TANTALUM COMPOUNDS). The ores are decomposed and separated by fractional crystallization of the double fluorides, fractional distillation of the pentachlorides, or by solvent extraction of the HF-containing solutions. The metals are prepared mainly by alkali metal reduction or fusion electrolysis

of the halides.

Tantalum carbide is produced by carburization of the element or the oxide with carbon, in a manner similar to the preparation of WC or TiC. Final carburization in a vacuum gives a golden yellow carbide, free of oxygen and nitrogen, that contains 6.1–6.3 wt % C and 0–0.2 wt % graphite.

The McKenna menstruum carburization process (7) for preparation of TaC parallels that for menstrum-made WC. The golden colored crystals produced have a specific gravity of about 14.2 and a bound-carbon content of 6.2–6.3 wt %. Starting material may be low niobium tantalite or microlite concentrates or high purity tantalum scrap. Low levels of niobium carbide in solid solution with TaC occur when tantalite is used and is of economic benefit, as NbC is widely used as a partial substitute for TaC in cemented carbide manufacture. The properties of TaC are given in Table 1; the Ta–C phase diagram is shown in Figure 3.

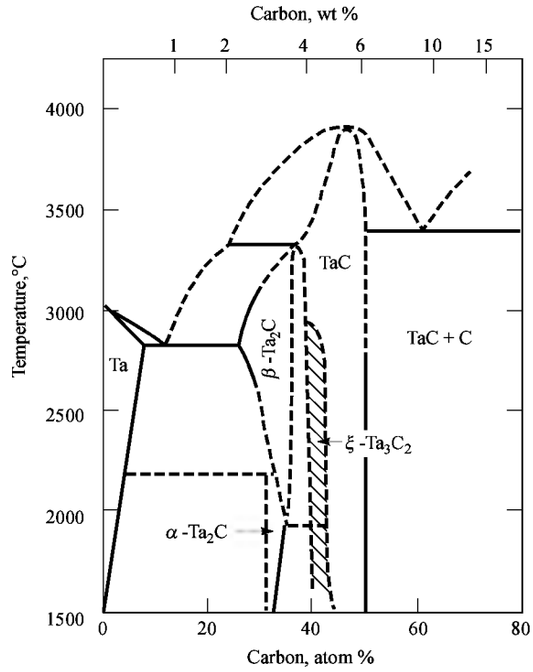

Fig. 3. Phase diagram for Ta–C.

WC–TiC–Co grades originally developed for machining long-chip materials have been largely replaced by WC–TiC–TaC(NbC)–Co grades that show higher hot-hardness and better thermal-shock resistance. This, as well as the addition of small (0.5–2 wt %) quantities of TaC to straight WC–Co alloys to prevent grain growth, has created a market for TaC. Annual world consumption of TaC(NbC) is estimated at 250–350 metric tons. Because of its high melting point, small quantities of TaC are used in high pressure lamps and as barriers between tungsten and graphite in rocket nozzles.

Niobium Carbide

The preparation of niobium *[7440-03-1]*, Nb, metal and niobium pentoxide *[1313-96-8]*, Nb_2O_5, is very similar to that of tantalum (see NIOBIUM AND NIOBIUM COMPOUNDS). Niobium carbide is prepared most often by the carburization of Nb_2O_5 with carbon black, and less frequently by reaction of niobium and carbon. The preparation of NbC has special importance because it is used on an industrial scale as a reducing agent to prepare niobium metal. In this process, finely divided mixtures of Nb_2O_5 and carbon black are pressed into cylindrical blocks in large hydraulic presses and converted to NbC in high frequency furnaces in the presence of hydrogen or under vacuum at 1600–1800°C. The carbide may then be mixed with further quantities of the oxide in induction-heated vacuum furnaces and processed to technical-grade niobium metal containing 1–3 wt % O_2, 0.5–1 wt % free graphite.

The menstruum niobium–carbide process (7) utilizes either columbite *[1310-23-2]* mineral concentrates or ferroniobium as starting materials. A low level of TaC in solid solution with NbC commonly occurs, as Ta and Nb occur together in ores. The properties of NbC are given in Table 1. The grayish brown NbC powder is used in cemented carbides to replace TaC. TaC–NbC solid solutions that have 3:1, 2:1, 1:1, and 1:2 ratios and the corresponding ternary and quaternary solid solutions with TiC and WC are common.

Auxiliary Carbides

Chromium Carbide. Cr_3C_2, the chromium carbide having the highest carbon level, is used as an additive in the preparation of cobalt or nickel-cemented WC or TiC-based carbide alloys designed for corrosion-resistant applications (see CORROSION AND CORROSION CONTROL). Lower carbon forms, eg, chromium carbide (7:3) *[12075-40-0]*, Cr_7C_3, are not suitable for these purposes. However, Cr_3C_2 is unstable in cobalt or nickel cemented alloys, tending to react with binder metals to produce brittle binary carbides. Lower carbon chromium carbides, however, are useful in reducing binder attack in corrosive applications. Chromium carbide is also used in cemented alloys as a grain-growth inhibitor.

Chromium carbide can be best prepared from pure chromic oxide *[1308-38-9]*, Cr_2O_3 (see CHROMIUM COMPOUNDS). Compacts containing 74 wt % Cr_2O_3 and 26 wt % carbon black can be heated in carbon-tube furnaces at 1600°C in the presence of hydrogen, giving a carbide containing 13–13.3 wt % total C and 0.1–0.3 wt % free C.

Chromium carbide is important in powder preparations designed for thermal spray applications of corrosion and wear-resistant coatings on tool and machine parts. Lower carbon carbides of chromium are important in hardfacing rods and electrodes for weld-applied overlays on machine wear surfaces. However, these carbides are usually formed *in situ* from Cr and C in the rod and not added as preformed carbides. The properties of Cr_3C_2 are listed in Table 2.

Table 2. Physical Properties of Auxiliary Carbides

Property	Cr_3C_2	β-Mo_2C	η-MoC	VC	HfC	ZrC
mol wt	180.05	203.91	107.96	62.96	190.51	103.23
carbon, wt %	13.33	5.89	11.3	19.08	6.30	11.64

crystal structure[a]	rhom, $D5_{10}$	hex, L′3	hex, L′3	fcc, B1	fcc, B1	fcc, B1
lattice constants, nm	a = 1.147 b = 0.554 c = 0.283	a = 0.300 c = 0.4734	a 0.298 c 0.281	0.4165	0.4648	0.4698
density, g cm^3	6.68	9.18	9.15	5.36	12.3	6.46
microhardness, kg mm^2	1350	1500	2200	2900	2600	2700
modulus of elasticity, N mm^2[b]	373,000	533,000		422,000	352,000	348,000
mp, °C	1810	2520	2600	2684	3820	3420
coefficient of thermal expansion, K ^{1}	10.3 × 10 ^{6}	7.8 × 10 ^{6}		7.2 × 10 ^{6}	6.59 × 10 ^{6}	6.73 × 10 ^{6}
heat of formation $\Delta H_{f,298}$, kJ mol[c]	94.2	49		124.8	230.3	196.8
specific heat, J (mol·K)[c]	32.7	30.3		32.3	37.4	37.8
electrical resistivity, $\mu\Omega$·cm	75	71		60	37	42
superconducting temperature, <K	<1.2	2.78		<1.2	<1.2	<1.2
Hall constant, cm^3 (A·s)	0.47 × 10 ^{4}	0.85 × 10 ^{4}		−0.48 × 10 ^{4}	−12.4 × 10 ^{4}	−9.42 × 10 ^{4}
magnetic susceptibility				+28	25.2	23

[a] rhom rhombohedral, hex hexagonal, fcc face-centered crystalline.

[b] To convert N mm^2 (MPa) to psi, multiply by 145.

[c] To convert J to cal, divide by 4.184.

Molybdenum Carbide. Mo_2C can be prepared by the carburization of molybdenum trioxide *[1313-27-5]*, MoO_3, and molybdenum dioxide *[18868-43-4]*, MoO_2, with carbon black or, more conveniently, by the reaction of molybdenum *[7439-98-7]*, Mo, powder (93.4 wt %) and carbon black or charcoal (~6.6 wt%) at 1350–1500°C, in the presence of hydrogen (see MOLYBDENUM AND MOLYBDENUM ALLOYS). The carbide formed contains 5.9–6.1 wt % total C and 0.05–0.25 wt % free C. The physical properties are listed in Table 2. There are two molybdenum carbides having higher carbon contents, ie, the cubic $MoC_{1\ x}$, a high temperature phase often described as Mo_3C_{2+x}, and the hexagonal η-molybdenum carbide *[12011-97-1]*, MoC, a low temperature phase. Both carbides tend to decompose to graphite and β-molybdenum carbide (2:1) *[12069-89-5]*, Mo_2C. The latter can be stabilized by W (8), N (9), or W + N (10) so that (Mo,W)C (11) or (Mo,W)(C,N) (10) mixed crystals are formed.

Molybdenum carbide is also used in TiC–Ni-based alloys and in titanium carbonitride-based cermets for metal-cutting applications.

Vanadium Carbide. Vanadium pentoxide *[1314-62-1]*, V_2O_5, or vanadium trioxide *[1314-34-7]*, VO_3, are the most satisfactory oxides for the preparation of VC. Vanadium pentoxide is best prepared by igniting chemically pure ammonium vanadate *[7803-55-6]*, NH_4VO_3, in the presence of moist oxygen to avoid reaction with nitrogen; V_2O_3 is obtained by reduction of V_2O_5 with hydrogen (see VANADIUM COMPOUNDS).

Vanadium carbide is prepared by the reaction of the elements under vacuum. In this process V_2O_5 is reduced at a high temperature with calcium *[7440-70-2]* and the product is melted in an arc furnace in the presence of argon producing a 99.9% pure material. Vanadium powder of equal purity may be prepared by hydriding and crushing vanadium metal turnings. Vacuum carburization removes nitrogen and oxygen, which are generally present up to 0.5–1 wt % in carbides obtained from vanadium oxides. The properties of VC are given in Table 2.

Although VC is very hard, it is very brittle and has, therefore, been used only in special cemented carbides. For example, submicrometer straight WC–Co alloys are prepared using ~0.5 wt% VC as a grain-growth inhibitor. TiC–VC–Ni–Fe cemented carbides were used in Germany during World War II as tungsten carbide–cobalt-free cutting tool alloys. Small quantities of VC are sometimes used in TiCN–Ni-based cermets.

Hafnium Carbide. The need of pure zirconium *[7440-67-7]* for nuclear reactors prompted the large-scale separation of hafnium *[7440-58-6]* from zirconium. This in turn made sufficient quantities of hafnium dioxide *[12055-23-1]*, HfO_2, or Hf metal sponge available for production of HfC for use in cemented carbides (see HAFNIUM AND HAFNIUM COMPOUNDS).

Hafnium carbide can be prepared industrially from hydrided hafnium sponge at 1500–1700°C or from HfO_2 at 2000–2200°C by carburization in vacuum in the presence of hydrogen. The resulting carbide contains almost the theoretical quantity of carbon, 6.30 wt % C, of which a maximum of 0.1 wt % is unbound.

The properties of HfC are listed in Table 2. Addition of HfC as NbC–HfC or TaC–HfC solid solutions to WC–TiC–Co alloys has been shown to improve the hardness (12).

Zirconium Carbide. ZrC may be prepared by igniting a mixture of 78.8 wt % annealed zirconium oxide *[1314-23-4]*, ZrO_2, and 21.2 wt % charcoal under hydrogen in a graphite crucible in a carbon-tube furnace at 2400°C. The carbide obtained has the following composition: 11.3 wt % chemically bound C, traces of free C, 88.3 wt % Zr, and 0.3 wt % (O_2 + N_2). Alternatively, a pressed mixture of ZrO_2 and carbon black may be induction-heated in a graphite crucible in the presence of H_2 at 1800°C, and then comminuted and annealed at 1700–1900°C, under vacuum, after addition of 1–2 wt % carbon black. The product contains 11.8 wt % C (~0.5 wt% free C).

The physical properties of ZrC are listed in Table 2. Zirconium carbide is much less important than TiC for cemented carbides.

Carbides of the Actinides, Uranium, and Thorium. The carbides of uranium and thorium are used as nuclear fuels and breeder materials for gas-cooled, graphite-moderated reactors (see NUCLEAR REACTORS). The actinide carbides are prepared by the reaction of metal or metal hydride powders with carbon or preferably by the reduction of the oxides uranium dioxide *[1344-57-6]*, UO_2, triuranium octaoxide *[1344-59-8]*, U_3O_8, or thorium dioxide *[1314-20-1]*, ThO_2, at 1800–2200°C in carbon-tube furnaces in the presence of hydrogen or in vacuum furnaces. Hot pressing and arc melting are very suitable methods for the preparation of homogeneous compacts, especially if followed by heat treatment in a tungsten-tube furnace in the presence of argon.

The properties of the uranium carbide *[12070-09-6]*, UC, uranium carbide (1:2) *[12071-33-9]*, thorium carbide *[12012-16-7]*, ThC, and thorium carbide (1:2) *[12071-31-7]*, ThC_2, are given in Table 3; the phase diagram for the system U–C is shown in Figure 4. Coefficient of thermal expansion for UC is 9.1 × 10 ^{6} K ^{1}, and its thermal conductivity is 25 W (m·K).

Table 3. Physical Properties of Uranium and Thorium Carbides

Property	UC	UC_2	ThC	ThC_2
mol wt	250.08	262.09	244.06	256.07
carbon, wt %	4.8	9.16	4.92	9.37
crystal structure[a]	fcc, B1	tetr, C11a	fcc, B1	mon
lattice constants, nm	0.49597	a = 0.3524 c = 0.5996	0.5346	a = 0.6691 b = 0.4231 c = 0.6744 β = 103°50′
density, g cm^3	13.63	11.86	10.64	8.65
microhardness, kg mm^2	920	620	850	600
mp, °C	2560	ca 2500	2625	2655

heat of formation, ΔH_{f298}, kJ mol[b]	97.1	96.3	29.3	125.2
specific heat, J (mol·K)[b]	50.2	58.6		
electrical resistivity, $\mu\Omega$·cm	40	90	25	30
magnetic susceptibility	+3.15	+3.40		

[a] tetr = tetragonal; mon = monoclinic; cubic.

[b] To convert J to cal, divide by 4.184.

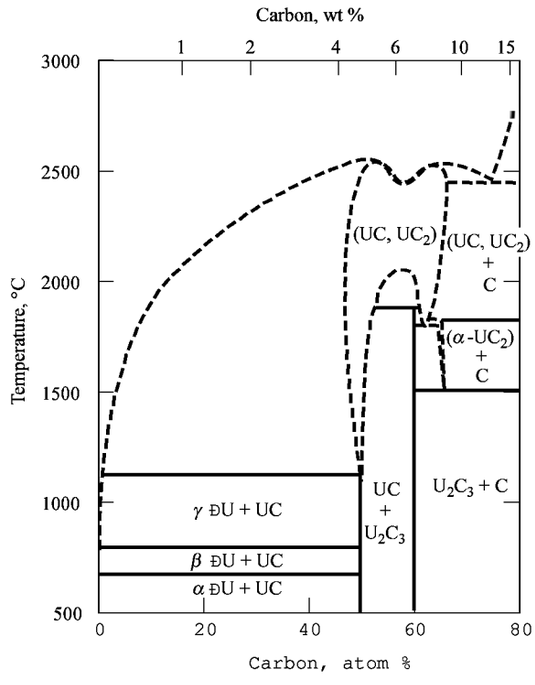

Fig. 4. Phase diagram for U–C.

Uranium carbide, UC, is comparatively stable whereas UC_2, especially in powder form, hydrolyzes rapidly in moist air. The latter is used in the form of pellets or annealed spherical particles, coated with pyrographite, as a nuclear fuel for high temperature reactors. For breeder reactors using thorium *[7440-29-1]*, it should be noted that UC and ThC form a continuous series of solid solutions, whereas UC_2 and ThC_2 have limited mutual solubility. Furthermore, UC can be stabilized with regard to its carbon content, even at high temperatures, by the formation of solid solutions with ZrC, HfC, NbC, or TaC so that no higher carbides are formed (13). Uranium carbides and plutonium carbides show a high degree of mutual miscibility (see ACTINIDES AND TRANSACTINIDES).

Carbides of the Iron Group Metals. The carbides of iron, nickel, cobalt, and manganese have lower melting points, lower hardness, and different structures than the hard metallic materials. Nonetheless, these carbides, particularly iron carbide and the double carbides with other transition metals, are of great technical importance as hardening components of alloy steels and cast iron.

The iron–carbon system contains the orthorhombic iron carbide (3:1) *[12011-67-5]*, Fe_3C, which melts congruently and represents the cementite in steel metallurgy. The existence of other carbides, eg, iron carbide (2:1) *[12011-66-4]*, Fe_2C, iron carbide (5:2) *[12127-45-6]*, Fe_5C_2, and iron carbide (7:3) *[12075-42-2]*, Fe_7C_3, is doubtful (see STEEL).

Iron carbide (3:1), Fe_3C; mol wt 179.56; carbon 6.69 wt %; density 7.64 g cm^{-3}; mp 1650°C; is obtained from high carbon iron melts as a dark gray air-sensitive powder by anodic isolation with hydrochloric acid. In the microstructure of steels, cementite appears in the form of etch-resistant grain borders, needles, or lamellae. Fe_3C powder cannot be sintered with binder metals to produce cemented carbides because Fe_3C reacts with the binder phase. The hard components in alloy steels, such as chromium steels, are double carbides of the formulas $(Cr,Fe)_{23}C$, $(Fe,Cr)_7C_3$, or $(Fe,Cr)_3C_2$, that derive from the binary chromium carbides, and can also contain tungsten or molybdenum. These double carbides are related to η-carbides, ternary compounds of the general formula $M_3M'_3C$ where M = iron metal; M′ = refractory transition metal.

The complex iron carbonitride is the hard component in steels that have been annealed with ammonia (nitrided steels). Complex carbonitrides with iron metals are also present in superalloys in the form of precipitates.

In the nickel–carbon and cobalt–carbon systems, the nickel carbide (3:1) *[12012-02-1]*, Ni_3C, and cobalt carbide (3:1) *[12011-59-5]*, Co_3C, are isomorphous with Fe_3C and exist only at low temperatures. The manganese–carbon system contains manganese carbide (3:1) *[12121-90-3]*, Mn_3C, isomorphous with Fe_3C, and manganese carbide (23:6) *[12266-65-8]*, $Mn_{23}C$, isomorphous with chromium carbide (23:6) *[12105-81-6]*, $Cr_{23}C$. These binary carbides occur frequently in the form of carbide solid solutions or double carbides with other transition metals in alloy steels, superalloys, and special hard metals.

Solid Solutions. Pure WC is of paramount importance in straight WC–Co alloys for machining short-chip materials and for a host of nonmetal-cutting applications. Fine-grained, straight WC–Co grades perform better than alloy carbides when cutting superalloys even though the superalloys produce long chips. For machining steels, alloyed carbides containing WC, Co, and binary and ternary solid solutions of the type WC–TiC, WC–TaC(NbC), WC–TiC–TaC(NbC), Ti(C,N), and (W,Mo)(C,N) are used. Solid solutions of titanium carbide and titanium nitride are used in cemented carbonitride cermet compositions for metal cutting applications.

The development of coatings (qv) of unalloyed, refractory carbides, nitrides, carbonitrides, and oxides on cemented carbide cutting tools has, in many cases, lessened the need for cubic solid-solution carbides in metal-cutting compositions. The solid solutions are harder and more heat-resistant than the pure components, and are substantially free from oxygen, nitrogen, and graphite because they are subjected to a type of autopurification during the diffusion annealing of the solid solutions. The vacuum-purified carbide solid solutions of the metals of Groups 4 (IVB), 5 (VB), and 6 (VIB) are wetted more readily by cobalt than are the unalloyed cubic carbides; they are also tougher.

The solid solutions of the carbides are generally prepared as are the pure carbides.

Carburization. Metal oxide mixtures with carbon black having additives such as Co, Ni, Fe, or Cr(0.5–1%) to promote diffusion, may undergo

carburization.

$$WO_3 + TiO_2 + C \xrightarrow[H_2,\ CO]{1600-1800^\circ C} (W,Ti)C + CO$$

$$WO_3 + TiO_2 + Ta_2O_5 + C \xrightarrow[H_2]{1600-1800^\circ C} (W,Ti,Ta)C + CO$$

$$MoO_3 + WO_3 + C + (Fe,Ni,Co) \xrightarrow[CO,\ H_2,\ CH_4]{1000-1200^\circ C} (Mo,W)C + CO + (Fe,Ni,Co)$$

Metal powder mixtures with carbon black may also undergo carburization.

$$W + Ta + C \xrightarrow[H_2,\ \text{vacuum}]{1500-1600^\circ C} (W,Ta)C$$

$$Hf + Ti + C \xrightarrow[H_2,\ \text{vacuum}]{1600-1800^\circ C} (Hf,Ti)C$$

Diffusion Annealing. Mixed preformed carbides can be diffusion-annealed at temperatures giving solid solutions. Additives, such as Co, Ni, Fe, or Cr (0.5–1%) promote diffusion.

$$WC + TiC \xrightarrow[H_2,\ \text{vacuum}]{1600-1900^\circ C} (W,Ti)C$$

$$WC + TiC + TaC(NbC) \xrightarrow[H_2,\ \text{vacuum}]{1600-1800^\circ C} (W,Ti,Ta,Nb)C$$

$$HfC + TiC + WC \xrightarrow[H_2\ \text{vacuum}]{1600-1900^\circ C} (Hf,Ti,W)C$$

$$TiN + TiC \xrightarrow[\text{vacuum}]{1600-1800^\circ C} Ti(C,N)$$

Menstruum Carburization. Mineral concentrates, ferroalloys, primary metals, or high purity scrap may also be carburized (14).

$$Fe(Mn)WO_4 + TiO_2 + Fe + C \xrightarrow{2300-2600^\circ C} (W,Ti)C + Fe(Mn) + Fe + CO + C$$

$$WFe + TiFe + C \xrightarrow{2300-2600^\circ C} (W,Ti)C + Fe + C$$

$$(Fe,Mn)(Ta,Nb)_2O_6 + Fe + C \xrightarrow{2300-2600^\circ C} (Ta,Nb)C + Fe(Mn) + Fe + CO + C$$

The monocarbides of Groups 4 (IVB) and 5 (VB) metals are completely miscible except for ZrC–VC and HfC–VC (Fig. 5). At 1400–1500°C, WC is soluble in the carbides of Groups 4 (IVB) and 5 (VB) 25–60 wt % , and at higher (1800–2400°C) temperatures even up to 90 wt % (15,16). WC itself, like the other carbides of Group 6 (VIB), has practically no solubility for face-centered cubic carbides. The cubic solid solutions, which are saturated at higher temperatures and contain a high percentage of WC, are very stable. The hexagonal WC forms complete series of solid solutions with the hexagonal MoC.

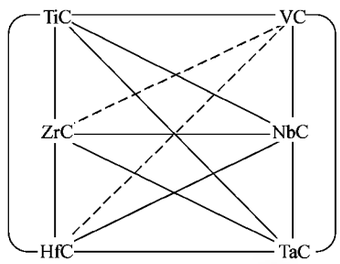

Fig. 5. Schematic illustrating the solid solubility between carbides. Solid line complete solubility; dashed line limited solubility.

The pseudoternary system WC–TiC–TaC is especially important in the metallurgy of cemented carbides (17). Figure 6 shows the phase distribution and thus the solubility ratios at 1450°C, which is the typical cemented carbide sintering temperature; at 2200°C, which is the preferred temperature for the formation of pure solid solutions having high WC content; and at 2500°C showing a hypothetical curve, maximum solubility. It is obvious that TiC is a better solvent for WC than TaC, ie, TaC additives in ternary solid solutions reduce the solubility for WC. The more spherical TiC–TaC–WC solid-solution grains can be readily distinguished from the angular WC in the microstructure.

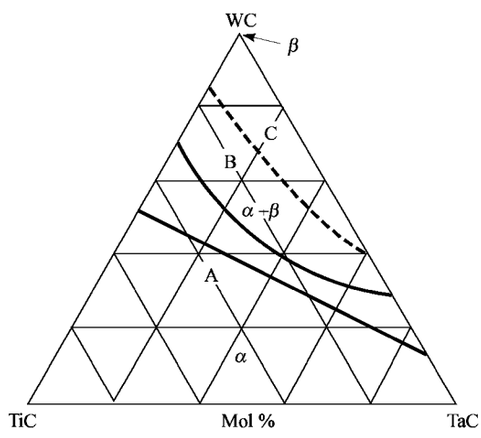

Fig. 6. Phase distribution in the system WC–TiC–TaC at A, 1450°C; B, 2200°C; and C, 2500°C. Dashed line hypothetical solubility; solid line experimental solubility.

Carbonitrides. Use of carbonitrides in metal cutting tools, both Ti(C,N) coatings (18) and Ni–Mo cemented carbonitrides (19), is expected to increase in the 1990s.

Complex Carbides. Complex carbides are ternary or quaternary intermetallic phases containing carbon and two or more metals. One metal can be a refractory transition metal; the second may be a metal from the iron or A-groups. Nonmetals can also be incorporated.

Complex carbides are very numerous. Many newer compounds of this class have been discovered and their structures elucidated (20). The octahedron M C is typical where the metals arrange around a central carbon atom. The octahedra may be connected via corners, edges, or faces. Trigonal prismatic polyhedra also occur. Defining *T* as transition metal and *M* as metal or main group nonmetal, the complex carbides can be classified as: (*1*) T_3M_2C, which has a filled β-manganese structure, eg, Mo_3Al_2C, W_3Re_2C; (*2*) T_2MC, *H*-phases, eg, Cr_2AlC, Ta_2GaC, Ti_2SC; (*3*) T_3MC, perovskite carbides which have the filled Cu_3Au-structure, eg, Ti_3AlC, VRu_3C, URh_3C; (*4*) T_3M_3C, T_2M_4C, η-carbides which have the filled Ti2Ni structure, eg, Co_3W_3C, Ni_2Mo_4C; and (*5*) κ-carbides, eg, $W_9Co_3C_4$, $Mo_{12}Cu_3Al_{11}C$.

The preferred method for synthesis of complex carbides is the powder metallurgy technique. Hot-pressed powder mixtures must be subjected to prolonged annealing treatments. If low melting or volatile components are present, autoclaves are used.

The η-carbides are not specifically synthesized, but are of technical importance, occurring in alloy steels, stellites, or as embrittling phases in cemented carbides. Other complex carbides in the form of precipitates may form in multicomponent alloys or in high temperature reactor fuels by reaction between the fission products and the moderator graphite, ie, pyrographite-coated fuel kernels.

Test Methods and Quality Control

The preparation of carbides requires rigorous chemical and physical examinations to control the quality and properties of the final product. The carbon content is of primary interest. The determination is carried out in a current of oxygen with addition of fluxing metals that assist in liberating carbon in the oxide form; the CO_2 formed is determined by infrared detector or thermal conductivity cells. In order to determine the free carbon, the carbide is treated with HNO_3–HF and the free carbon is separated. Decomposition of some carbides, particularly SiC, B_4C, and Cr_3C_2, is troublesome. Nitrogen and oxygen determinations are carried out by inert gas fusion method.

For x-ray investigations, the diffractometer method is generally used. The lattice constants indicate purity or composition of solid solutions; the rapid counting-tube goniometric method can be used at the manufacturing plant for quality control. The rotating-crystal and neutron diffraction methods are sometimes used for structure elucidation.

The hardness of carbides can only be determined by micro methods; because of brittleness, the usual macro tests cannot be used. Neither can the extremely high melting points of the carbides be readily determined by the usual methods. In the so-called Priani hole method, a small hollow rod is placed between two electrodes and heated by direct current until a liquid drop appears in the cavity. The temperature is determined pyrometrically. When high temperature tungsten tube furnaces are used, the melting point can readily be estimated by the Seger-type cone method. The sample may also be fused in a Kroll arc furnace and the solidification temperature determined.

Economic Aspects

Two categories of refining support manufacturers of cemented carbides. The first involves extraction of tungsten in the form of tungstic oxide, WO_3, or ammonium paratungstate, APT, from mineral concentrates. The second converts the WO_3, APT, and other starting materials to primary carbides of tungsten and other metals. Some refining, especially the preparation of primary carbides, is carried out by the cemented carbide manufacturers themselves. Cemented carbide manufacturers also utilize independent refiners specializing in powders of primary metals, carbides, nitrides, carbonitrides, and many lower volume accessory materials used in cemented carbide production. These suppliers include Metallurg Inc., Hermann C. Starck, and Murex Ltd., among others.

A number of cemented carbide producers market some or all primary materials, ranging from monocarbides to binary or ternary solid solutions involving TiC, TaC, NbC, or WC. Among the suppliers offering these materials are Kennametal Inc., GTE Products Corp., Teledyne Wah Chang, and Tokyo Tungsten Co. Ltd. Kennametal Inc. also manufactures TiN and TiCN powders.

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CALCIUM CARBIDE

Chemically pure calcium carbide *[75-20-7]*, Ca_2C, is a colorless solid; however, the pure material can be prepared only by very special techniques. Commercial calcium carbide is composed of calcium carbide, calcium oxide *[1305-78-8]*, CaO, and other impurities present in the raw materials. The commercial product's calcium carbide content varies and is sold based on acetylene yield. Industrial-grade calcium carbide contains about 80% as CaC_2, 15% CaO, and 5% other impurities.

Calcium carbide was first made in the laboratory in the mid-1800s. Commercial production by the electric furnace method was developed about 1892 by Moissan in France and independently by Willson in the United States. Development of the carbide industry for generation of acetylene began in 1895 and expanded rapidly.

Originally used as an illuminant, acetylene *[74-86-2]*, C_2H_2, from carbide quickly found use in oxyacetylene welding (qv) and cutting, in the production of calcium cyanamide *[156-62-7]*, $CaCN_2$, and as a source of valuable organic chemicals during World War I (see ACETYLENE DERIVED CHEMICALS; HYDROCARBONS, ACETYLENE). Increased acetylene usage for the production of organic chemicals, resins, and plastics increased the demand for calcium carbide. Annual production in the United States reached a maximum of 1,027,000 metric tons in 1964, whereupon production declined substantially as acetylene from carbide was replaced by acetylene from petrochemical sources (see FEEDSTOCKS), the thermal cracking of hydrocarbons (qv), and as a by-product in ethylene (qv) production. From 1975 to 1988 calcium carbide production ranged from 175,000 to 253,000 t yr.

In the United States calcium carbide-based acetylene is mainly used in the oxyacetylene welding market although some continues to be used for production of such chemicals as vinyl ethers and acetylenic alcohols. Calcium carbide is used extensively as a desulfurizing reagent in steel and ductile iron production allowing steel mills to use high sulfur coke without the penalty of excessive sulfur in the resultant steel (see SULFUR REMOVAL AND RECOVERY). Calcium cyanamide production continues in Canada and Europe (see CYANAMIDES).

Properties

Table 1 lists the more important physical properties of calcium carbide. Additional properties are given in the literature (1). Figure 1 gives the phase diagram calcium carbide–calcium oxide for pure and technical grades.

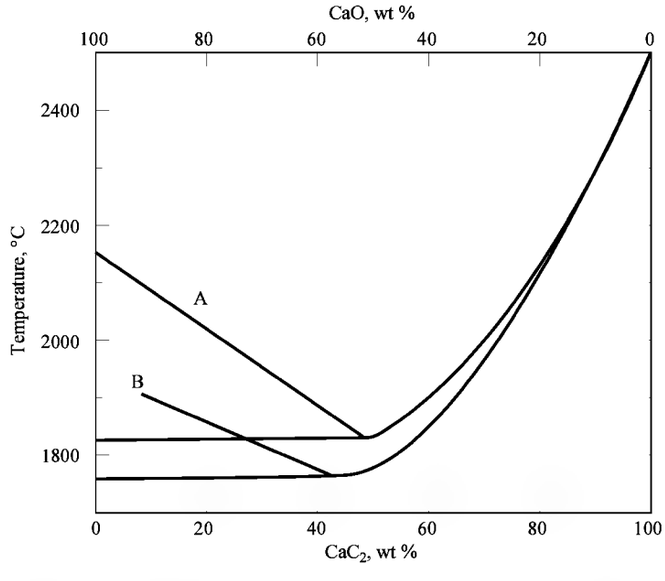

Fig. 1. Calcium carbide–calcium oxide phase diagram using A, pure CaC_2, and B, technical-grade CaC_2.

Table 1. Physical Properties of Calcium Carbide

Property	Value
mol wt	64.10
mp, °C	2300
crystal structure	
phase I, 25–447°C	face centered tetragonal
phase II, <25°C	triclinic
phase III[a]	monoclinic
phase IV, >450°C	fcc
commercial	grain structure, 7–120 μm
specific gravity, commercial-grade	
at 15°C	2.34
2000°C[b]	1.84
electrical conductivity, technical-grade, (ohm-cm)[1]	
at 25°C	3,000–10,000
1000°C	200–1,000

1700°C[b]	0.36–0.47
1900°C[b]	0.075–0.078
viscosity at 1900°C, MPa·s (CP)	
50% CaC_2	6000
87% CaC_2	1700
specific heat, 0–2000°C, J mol·K[c]	74.9
heat of formation, H_{f298}, kJ mol[c]	59 ± 8
latent heat of fusion, ΔH_{fus}, kJ mol[c]	32

[a] Phase III is metastable.

[b] Material is a liquid.

[c] To convert from J to cal, divide by 4.184.

Reaction With Water. The exothermic reaction of calcium carbide and water-yielding acetylene forms the basis of the most important industrial use of calcium carbide.

$$CaC_2 + 2\,H_2O \rightarrow C_2H_2 + Ca(OH)_2 \qquad \Delta H \quad 130\ \text{kJ mol} \ (\ 31.1\ \text{kcal mol})$$

Both wet and dry processes are in use for generating acetylene from calcium carbide. In the wet process, carbide is added to excess water in a generator, ie, one part by weight carbide to eight parts by weight water. Water absorbs the heat of reaction, maintaining the temperature below 100°C, and a 10% lime sludge slurry results as a waste product. In the dry process an equal amount of water is added to carbide at a rate such that the heat of reaction vaporizes the excess water. The by-product, calcium hydroxide *[1305-62-0]*, $Ca(OH)_2$, containing 2–3% water is a free-flowing powder that can be sold or returned to the carbide process, however it is generally not economical to return $Ca(OH)_2$ to the process. Both processes yield acetylene of 99.6% purity after a light scrubbing operation.

If there is a deficiency of water, or in the presence of partially slacked carbide, the reaction

$$CaC_2 + Ca(OH)_2 \rightarrow C_2H_2 + 2\,CaO$$

can occur. This reaction proceeds slowly at room temperature, appreciably at 110–120°C, and can occur in crushed carbide containing air-slacked material.

Reaction With Sulfur. An important use of calcium carbide has developed in the iron (qv) and steel (qv) industries where the carbide has been found to be an effective desulfurizing agent for blast-furnace iron. Calcium carbide and sulfur present in the molten metal react

$$CaC_2 + S \rightarrow CaS + 2\,C$$

Sulfur has been controlled in the iron and steel industries by careful selection of raw materials. Because the availability of high grade raw materials containing low levels of sulfur has declined, and in an attempt to maximize production rates, producers have shifted toward external desulfurization using additives such as calcium carbide in a separate step in the reduction process. Desulfurization by using nitrogen gas to inject calcium carbide powders into a ladle or torpedo car is both fast and efficient. Injection using a refractory nozzle below the metal surface reduces sulfur content from 0.1 to 0.01%. Other ingredients, such as calcium carbonate which acts as a gassing agent, or graphite which assists in the injection process, are generally added to the desulfurizing reagent. A magnesium desulfurizing reagent has also been used either as a blend with calcium carbide or in a sequential co-injection process (see SULFUR REMOVAL AND RECOVERY).

Reaction With Nitrogen. Calcium cyanamide is produced from calcium carbide

$$CaC_2 + N_2 \rightarrow CaCN_2 + C \qquad \Delta H \quad 295\ \text{kJ mol} \ (\ 70.5\ \text{kcal mol})$$

The reaction is carried out in a refractory oven by passing nitrogen gas through finely pulverized carbide at a temperature of 1000–1200°C. To initiate the reaction, the carbide is heated electrically using a graphite electrode located at the center of the charge. Because the reaction is strongly exothermic, it proceeds autogenously. In addition to the batch-oven process, some European and Japanese producers have developed continuous nitrogenation furnaces based on a rotary kiln design. Powdered carbide and nitrogen gas is fed to the kiln and the cyanamide product removed in a granular form.

Manufacture

Calcium carbide is produced commercially by reaction of high purity quicklime and a reducing agent such as coke in an electric furnace at 2000–2200°C.

$$CaO + 3\,C \rightarrow CaC_2 + CO \qquad \Delta H = 466\ \text{kJ mol} \ (111\ \text{kcal mol})$$

Commercial calcium carbide, containing about 80% CaC_2, is formed in the liquid state. Impurities are mainly CaO and impurities present in raw materials. CO is usually collected for use as a fuel in lime production or drying of the coke used in the process. The liquid calcium carbide is tapped from the furnace into cooling molds.

Raw Materials. The basic raw materials limestone and coke or coal (qv) should be high quality. Limestone should contain a minimum of 95–97% $CaCO_3$ and a maximum of 1.5% $MgCO_3$, 1–1.5% SiO_2, 1% Fe_2O_3 plus Al_2O_3, and 0.006% phosphorus (see LIME AND LIMESTONE). The limestone is first converted to lime in a rotary or vertical shaft kiln. The lime is screened to eliminate fines that interfere with the evolution of carbon monoxide in the smelting process.

If acetylene is produced on-site, recycle of the lime hydrate can save both raw material and disposal costs. The usual route involves centrifuging the wet generator sludge, calcining the centrifuge cake, and briquetting the resulting lime. Dry generator lime hydrate can be briquetted and charged directly to a lime kiln. Up to 33% of the total lime charge can be replaced by recycle material, however this is limited by a buildup of impurities to a level where furnace operation is impeded. Lime fines obtained by screening can be briquetted and used with the furnace charge or used as a feed in the hollow electrode system.

The carbon-reducing agent can be metallurgical coke, petroleum coke, or anthracite depending on price and impurities. Coke is the most common because of availability. Petroleum coke is desirable because of low ash content and high resistivity. Anthracite can be used, however, it is not preferred as a result of its low reactivity. Charcoal is successfully used in South America. Metallurgical coke typically contains 85–88% fixed carbon, 9–11% ash, and 2% volatiles. The main ash impurities are SiO_2 (50%) and the balance Al_2O_3 and Fe_2O_3. Received coke contains 15% moisture and is dried to 1% before being charged to the furnace. It is screened to a 25 × 6 mm-sized fraction.

Large quantities of fines in the furnace charge cause furnace blows that are hazardous to operator and equipment. Blows result when the steady flow of mix to part of the melt zone is stopped by a fines bridge; the calcium carbide liquid overheats and then dissociates at 2250°C.

$$CaC_2 + 2\,CaO \rightarrow 3\,Ca(g) + 2\,CO(g)$$

The 2.5-fold increase in gas generation causes the mix burden to give away as hot gases and liquid erupt from the furnace hearth.

Because of the high temperatures and strong reducing conditions in the furnace a number of energy-consuming reactions take place. Silica, the main impurity in the raw materials, may be partly volatilized as silicon and later reoxidized in the cooler parts of the furnace. Some is reduced and combines with

iron present to form a ferrosilicon alloy; some reacts with carbon to form silicon carbide, or with lime to form calcium silicate. Alumina forms a soluble calcium aluminate. Magnesia is reduced to metallic magnesium and reoxidized in the cooler part of the furnace. Eventually 80–90% is flushed from the smelting zone by the evolved carbon monoxide. Sulfur and phosphorus remain largely with the carbide as calcium sulfide and calcium phosphide.

The carbide impurities tend to distill and are reoxidized in the upper, cooler region of the charge. This process forms crusts near the top of the charge or around the cooler part of the reaction crucible and causes trouble in furnace operation. Large amounts of dissolved calcium silicate and aluminate may form a viscous melt and impede the tapping process. Ferrosilicon is commonly removed from the crushed carbide by electromagnets.

Hollow Electrode. Coke and lime fines, conveyed in a stream of recycle furnace gas or nitrogen, can be fed to the furnace through a 10–15-cm pipe channel at the center of each Soderberg electrode. Although the steel pipe melts and disappears in the current carrying zone of the electrode, it remains intact long enough to maintain a continuous opening. Fines delivered to this zone react quickly and provide a valuable tool for adjusting carbide grade and maintaining proper electrical load balance. In addition to the economic gain of utilizing a waste material and eliminating a disposal problem, there is a 30% reduction in usage of electrode carbon. Approximately 15–20% of the total raw material charge can be introduced though the hollow electrodes. It is also possible to recycle calcium carbide dust, which is generated in the carbide crushing process.

Material and Energy Requirements. Material requirements per metric ton of carbide vary within moderate limits. On the basis of 95% available CaO in the lime and 88% fixed carbon in coke about 865 kg of lime and 494 kg of coke is required to produce a metric ton of calcium carbide of 80% purity.

Electrode consumption varies from 10–27 kg/t of carbide. The theoretical energy requirement per metric ton is about 2200 kW·h, but because of heat losses, 2800–3100 kW·h is required. For every metric ton of 80% purity carbide produced, about 280 m^3 (15°C) of furnace gas is evolved, which analyzes as 75–85% CO, 5–12% H_2, and the balance as N_2, CO_2, and CH_4.

Furnace Design. Modern carbide furnaces have capacities ranging from 45,000 t/yr (20 MW) to 180,000 t/yr (70 MW). A cross-section of a 40 MW furnace, constructed in 1981, having a 300 t/d capacity is shown in Figure 2. The shell consists of reinforced steel side walls and bottom. Shell diameter is about 9 m and the height to diameter ratio is shallow at 0.25:1.0. The walls have a refractory lining of 0.7 m and the bottom has a 1-m layer of brick topped by a 1.5-m layer of prebaked carbon blocks. The steel shell is supported on concrete piers and cooling air is blown across the shell bottom. A taphole to withdraw the liquid carbide is located at the top of the carbon blocks.

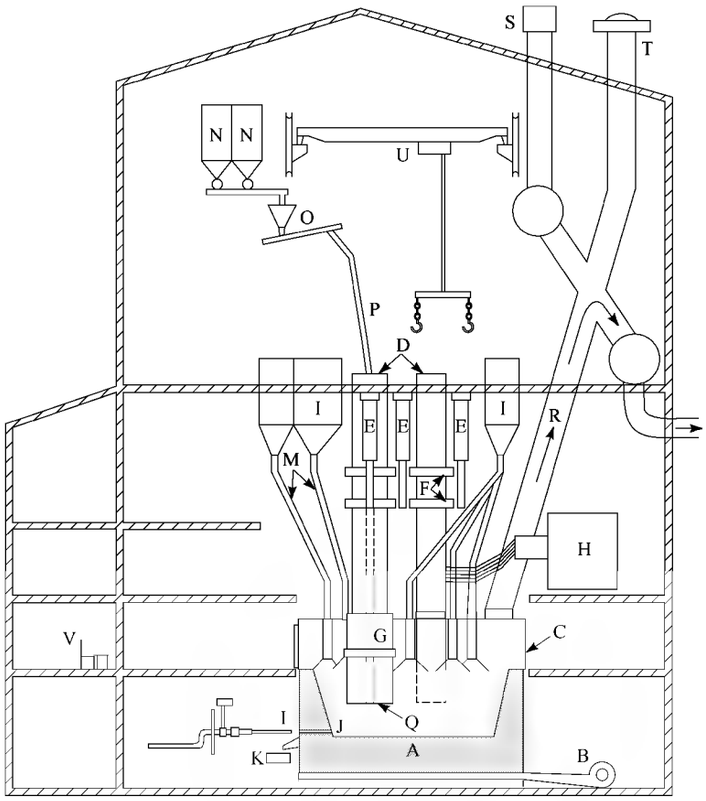

Fig. 2. A 300 t/d carbide furnace. The furnace crucible, A, is constructed of brick sidewalls, a carbon-lined bottom; the bottom being cooled by a fan, B. The entire furnace is closed by a cover, C. The Soderberg electrodes, D, are supported and can be moved vertically by hydraulic cylinders, E. They are fitted with a slipping device, F. Contact plates, G, provide power connection to the electrodes from a single-phase transformer, H. A tapping electrode, I, assists the flow of carbide from the taphole, J, to a tapping conveyor or chill car, K, Raw material is stored in bins, L, and introduced to the furnace through charging chutes, M, Dust raw material is stored in separate bins, N, and fed to the furnace via screw conveyor O, flexible connector P, through the hollow electrode Q. Furnace gas is removed through duct R. A chimney, S, and pressure relief device, T, are for emergency use. A crane, U, charges fresh electrode paste. An operator monitors operation from a control room, V.

The furnace cavity is completely closed and relatively gas-tight. The electrodes enter the furnace through water-cooled sealing devices in the cover. Furnace charge enters through water-cooled charge tubes. Carbon monoxide gas is drawn off by a fan through a large water-cooled pipe. The gas pressure under the cover is slightly below atmospheric and is controlled by a pressure regulator.

Electrodes. Continuous self-baking Soderberg electrodes, such as the one shown in Figure 3, are used in modern carbide furnaces. They are arranged in triangular layout and consist of light-gauge steel casing suspended vertically above the furnace. The casing, which is reinforced with steel fins, is filled with Soderberg paste, a formulated mixture of electrically calcined anthracite and coal-tar pitch (Fig. 4). The paste blocks or chunks become plastic at a temperature of 70°C and take the shape of the steel casing.

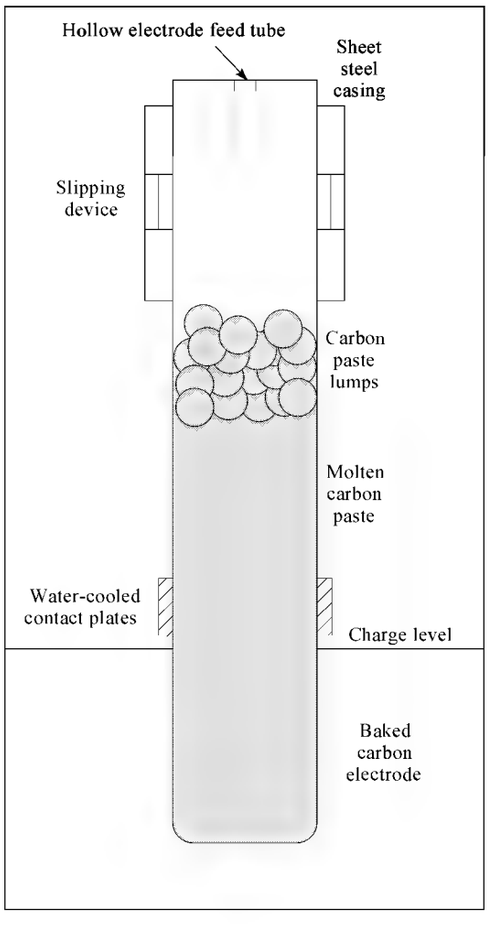

Fig. 3. Soderberg electrode.

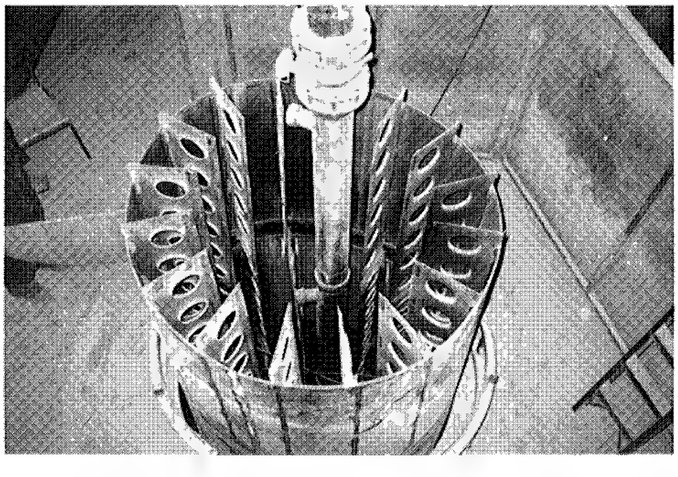

Fig. 4. Top view of Soderberg electrode showing reinforcing fins and steel casing with hollow electrode pipe at the center.

Baking of the paste to a dense amorphous carbon mass commences in the area just above electrical contact plates. Below the plates the casing disappears as a result of melting and oxidation leaving the baked paste as a monolithic carbon cylinder of considerable strength and electrical conductivity capable of carrying current to the charge melting zone.

Carbon in the electrode tip is continuously consumed during furnace operation. Replacement electrode is extruded by an operation called slipping. This is carried out by a pair of hydraulically tightened slipping bands mounted one above the other on the electrode column. The electrode is held by the lower set of bands allowing the upper set to be raised to a new position. On release of the lower bands the electrode can be lowered safely using the hydraulic cylinders provided for the upper bands. Normally the electrode is held in the stable position by the action of both bands. Depending on the current-carrying capacity required, Soderberg electrodes vary in diameter from 1100–1600 mm and are 15 m in casing length. Normal slipping rates average 2.5 cm h. The complete electrode assembly is suspended from a pair of hydraulic cylinders. Movement of the cylinders, which varies automatically with the resistance of the furnace charge, determines electrode penetration in the furnace.

Electrical Connections. Electric current is brought from the transformers by air-cooled copper busbars and close to the electrode by water-cooled bus tubes and flexible cables, connecting to water-cooled copper contact plates at the electrode. The plates are held against the electrode by hydraulic pressure. The connectors are as short and as balanced as possible to allow cancelling of magnetic fields associated with individual conductors.

Three single-phase transformers are used to step down from the high voltage supply to an operating voltage of 150–325 V. Power factor correction is carried out on the high voltage side using banks of capacitors. Provision of a Wye Delta switching system on the high voltage side of the transformer allows the operating voltage to be reduced for startups.

Furnace Operation. A crew of five is typically needed to operate a large carbide furnace installation; one person for raw material control, two for furnace operation, and two for tapping. The lime and coke are weighed separately by automatic weigh scales that discharge onto conveyors feeding the furnace area. The charge is delivered to the furnace continuously by feed conveyors that automatically maintain the charge levels in the feed pipes. As the

charge enters it is heated in the upper zones by radiation from the electrodes and by heat exchange from the carbon monoxide leaving the reaction area. The lime is melted in the reaction zone close to the electrode tip. The reaction zones are limited close to the area near the electrodes. Charge material outside this area does not react, but serves as a crucible liner.

At the upper level of the mix, coke and lime are relatively cold and incapable of carrying any current. At a distance of ca 30 cm below the surface the mix is hot enough to carry some current between electrodes. Penetration of the electrodes into the furnace is usually 90–125 cm. Mix at the electrode tip may reach 1600°C at which temperature conductivity is good but usually not sufficient to melt the lime.

Further down, ca 75 cm below the electrode tips, the mix is hot enough (2200–2500°C) to allow the lime to melt. The coke does not melt and the liquid lime percolates downward through the relatively fixed bed of coke forming calcium carbide, which is liquid at this temperature. Both liquids erode coke particles as they flow downward. The weak carbide first formed is converted to richer material by continued contact and reaction with coke particles. The carbon monoxide gas produced in this area must be released by flowing back up through the charge. The process continues down to the taphole level. Material in this area consists of solid coke wetted in a pool of liquid lime and liquid calcium carbide at the furnace bottom.

The ease with which carbon monoxide can escape from the reaction zone has an important bearing on smooth operation of the furnace. The normal furnace charge, consisting of large particles, has a good porosity allowing a reasonably constant gas flow. Extremely fine raw materials or crusts of condensed impurities impede the escape of gas from the reaction area, allowing pressure to develop and eventually result in "blows" in which hot mix and liquid carbide can be explosively ejected. As noted, a raw material fines bridge also results in overheating of liquid carbide and subsequent dissociation to calcium vapor and carbon monoxide. The resulting gas generation rate is more than double the normal rate and can cause an eruption from the hearth.

Metallurgical coke gives rise to ferrosilicon, which in the liquid phase is more dense than calcium carbide and tends to settle and penetrate the bottom of the furnace. After a lengthy operating period it may extend 30 cm or more below the taphole, eventually reaching the furnace shell where it causes hot spots requiring repair and replacement of the furnace refractory.

An evenly operating furnace is essential for an efficient process as indicated by steady electrode penetration in the charge as measured by the distance of the electrode tip above the taphole; regular descent of mix through all charging chutes; and regular tapping of liquid carbide equivalent to power input to the furnace. These conditions are attained by maintaining standard operating procedures, which include frequent and adequate tapping of carbide; constant electrical conditions and hence power input; and a constant coke to lime ratio in the charge mix.

Computer Control. The use of computer systems to control the operation of submerged arc furnaces, including calcium carbide, has been successfully demonstrated in the United States (see EXPERT SYSTEMS; PROCESS CONTROL). Operations directly under control are mix batching, electrode position and slip control, carbide gas yield, power control, and cooling water systems. Improvements in energy usage, operating time, and product quality are obtained.

Tapping System. Modern carbide furnaces are provided with a single taphole at one electrode, or three tapholes leading to the center of each electrode zone. When three tapholes are used, each electrode is tapped in turn usually at 20–40 min intervals, making the tapping process almost a continuous one. When a single taphole is used, a continuous flow of liquid carbide is maintained. Single taphole operation requires that the reaction zone under the three electrodes are joined, thereby forming a common pool of liquid melt. The taphole channel is opened by burning through the taphole with a tapping electrode. When the tip of the tapping electrode is applied to the hot solidified carbide, a circuit is completed with the electrodes in the furnace and sufficient heat quickly develops to melt the carbide and establish a flow of liquid carbide from the furnace. A pneumatic ram bar is also used to poke the taphole at regular intervals and promote the flow of liquid carbide.

Carbide is tapped from the furnace in a liquid stream at a temperature of 1900–2100°C. Its very low thermal conductivity makes it possible to tap directly into cast-iron chill cars even though the melting point of the cast iron is lower than that of the carbide. The liquid carbide may be: cast into chills yielding a pig weighing up to 4.5 t; cast onto smaller chills placed on a tapping wheel giving pigs of about 90 kg; tapped onto a self-discharging tapping conveyor, consisting of shallow metal pans mounted on a continuous-chain conveyor sufficiently long that the small ingot formed in each pan is solidified on reaching the discharge point; or tapped onto a slightly inclined water-cooled rotating cylinder.

In the last two methods the carbide is ready for crushing upon discharge from the conveyor or cylinder. In the first method the pigs must be cooled for several hours before removal from the chills and then cooled an additional 24–30 h before being crushed.

Crushing, Screening, and Packing. The solidified carbide is sometimes first broken by dropping the pig on a reinforced breaking table. Gyratory crushers capable of handling a large pig in one piece are also used. Crushed carbide is fed to a screening plant where the carbide is screened for packing according to preestablished screen sizes. Gyratory screens are the most effective for product screening. Magnetic separators are used to remove ferrosilicon to prevent damage to acetylene generators.

Calcium carbide used for desulfurization is milled to a powder in large multichamber ball or rod mills. Performance-enhancing ingredients such as limestone and graphite may be added during the milling process or added later in a post blending operation.

Calcium carbide for acetylene is mainly packed in returnable steel bulk containers ranging in capacity from 2.5–4.5 t, suitable for lift trucks and unloading conveyors. The granular carbide is lightly oiled with a lubricating oil (see LUBRICATION AND LUBRICANTS), which decreases the rate of reaction when exposed to moist air and also reduces dust formation during handling.

Environmental Considerations. The principal environmental problem is the prevention of particulate dust emission, which can be handled by cloth filtration equipment. Filtration of taphole fumes consisting of submicrometer particles, which rapidly clog the filtration media, is both difficult and expensive. Dust collectors operating at low air to cloth ratios are required. Dust created in material handling equipment is of relatively large particle size and easily handled by cloth filtration. Treatment of the furnace CO gas stream is complicated by the high temperature of the gas, its explosiveness, toxicity, dust concentration, and particle size.

Typical carbide furnace gas contains about 80% CO and small amounts of H_2, CO_2, N_2, and CH_4. Dust concentration depends on the raw material and varies from 225–450 g m^3. The gas temperature at point of discharge from the furnace cover is usually in the 650–800°C range.

Two methods are used to aspirate gas from the furnace to point of delivery for use as a fuel. Wet handling combines pumping, cooling, and scrubbing. Dry handling requires use of either a ceramic filtration device, which can be located near the furnace, or a high temperature fabric filter located a sufficient distance from the furnace to allow gas cooling during transport. The dust collected by either wet or dry methods may contain a trace of cyanide and must be treated before disposal.

Specifications and Shipping

Contracts for acetylene-grade carbide are usually based on size and gas yield specification, and include penalties for carbide that fails to meet specified gas yield. The sizes generally available in the trade are based on established U.S. Government specifications. In general gas yields range from 280–300 L kg and depend on the screen size of the carbide. The most important standard is the method of expressing gas yield, which in the United States is at 15°C and 101 kPa (1 atm). Gas impurities are typically 0.05% by volume phosphine, 0.15% by volume hydrogen sulfide, and 0.001% arsine.

Calcium carbide is classed as a hazardous chemical under Department of Transportation regulations. Domestic shipments are mainly in steel tote bins varying in capacity from 2.5–4.5 t. A small amount continues to be shipped in industrial wide mouth steel drums of 270 kg capacity. Containers must be marked "Flammable solid, dangerous when wet" and have the United Nations designation UN 1402.

Calcium carbide for desulfurization is usually sold on the basis of minimum CaC_2 content, minimum levels of various additives, and a specified size distribution. These designations can vary considerably based on the reagent formulation. Domestic shipments are in either steel tote bins of 2–4 t capacity, or bulk rail cars or trucks having pneumatic unloading capabilities. Containers are usually pressurized slightly with an inert gas such as dry nitrogen to avoid reagent contact with moist atmospheric air and generation of potentially explosive acetylene–air mixtures.

Analytical and Test Methods

Gas yield, the most important specification for acetylene-grade carbide, is determined by slaking the carbide in water, collecting and measuring the volume

of evolved acetylene, and converting to standard conditions. Phosphorus, sulfur and arsenic levels are checked by determining phosphine, hydrogen sulfide, and arsine content of the evolved acetylene according to specified procedures. Phosphine may be determined by absorption in iodine solution followed by precipitation of phosphomolybdate complex (see PHOSPHINE AND ITS DERIVATIVES). Sulfur and arsenic are determined by absorption in sodium hypochlorite solution followed by precipitation of barium sulfate in the case of sulfur (qv), and by acidification of the solution and volatilization of arsine by the Gutzeit procedure in the case of arsenic (see ARSENIC AND ARSENIC ALLOYS).

Health and Safety

The usual precautions must be observed around the high tension electrical equipment supplying power. The carbon monoxide formed, if collected in closed furnaces, is usually handled through blowers, scrubbers, and thence to a pipe transmission system. As calcium carbide exposed to water readily generates acetylene, the numerous cooling sections required must be constantly monitored for leaks. When acetylene is generated, proper precautions must be taken because of explosibility of air–acetylene mixtures over a wide range of concentrations (from 2.5 to 82% acetylene by volume) and the flammability of 82–100% mixtures under certain conditions.

Although acetylene is considered to be a material having a very low toxicity, a threshold limit value (TLV) of 2500 ppm has been established by NIOSH. In the presence of a small amount of water carbide may become incandescent and ignition of the evolved air–acetylene mixture may occur. Nonsparking tools should be used when working in the area of acetylene-generating equipment.

Economic Aspects

World production of calcium carbide is given in Table 2. The calcium carbide industry began a state of decline in the late 1960s when acetylene from carbide was gradually replaced by petrochemical starting materials. Calcium carbide usage for iron desulfurization began in the United States in the mid-1970s and today accounts for 18% of carbide production. Future growth in calcium carbide usage is expected to be modest. The 1990 market price of calcium carbide was about $515 t.

Table 2. World Production of Calcium Carbide, 10^3 t/yr

Country	1962	1972	1982	1988	1990
United States	982	447	175	225	236
Canada	318	73	75	90	80
Europe	4740	4710	3260		
Asia and Australia	1800	2000	2420		
Africa	60	80	250		
South America	100	190	220		

Uses

The largest use for calcium carbide is in the production of acetylene for oxyacetylene welding and cutting. Companies producing compressed acetylene gas are located near user plants to minimize freight costs on the gas cylinders. Some acetylene from carbide continues to compete with acetylene from petrochemical sources on a small scale. In Canada and other countries the production of calcium cyanamide from calcium carbide continues. More recently calcium carbide has found increased use as a desulfurizing reagent of blast-furnace metal for the production of steel and low sulfur nodular cast iron.

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SILICON CARBIDE

Silicon carbide *[409-21-2]*, SiC, is a crystalline material having a color that varies from nearly clear through pale yellow or green to black, depending on the amount of impurities. It occurs naturally only as the mineral moissanite *[12125-94-9]* in the meteorite iron of Canon Diablo, Arizona. The commercial product, which is made in an electric furnace, is usually obtained as an aggregate of iridescent crystals. The iridescence is caused by a thin layer of silica produced by superficial oxidation of the carbide. The loose black or green grain of commerce is prepared from the manufactured product by crushing and grading for size.

In 1891, a small amount of silicon carbide was produced by passing a strong electric current from a carbon electrode through a mixture of clay and coke contained in an iron bowl that served as the second electrode (1). The abrasive value of the crystals obtained were recognized and The Carborundum Company was founded that year (2). About 10 years earlier tetratomic radicals of silicon ($Si_2C_2O_2$, Si_2C_2N) had been reported (3). That work also produced some SiC.

Traditionally, the metallurgical, abrasive, and refractory industries are the largest users of silicon carbide (see ABRASIVES; METALLURGY; REFRACTORIES). SiC is also used for heating elements in electric furnaces (see FURNACES, ELECTRIC), in electronic devices, and in applications where its resistance to nuclear radiation damage is advantageous. The development of advanced pressureless sintering and complex shape-forming technologies has led to silicon carbide becoming one of the most important structural ceramics (see ADVANCED CERAMICS, STRUCTURAL CERAMICS). Silicon carbide has found wide acceptance in wear-, erosion-, and corrosion-resistant applications; it has demonstrated excellent performance as a heat-exchanger material; it is also being evaluated for prototype high temperature gas turbine engine component applications.

Properties

The properties of silicon carbide (4–6) depend on purity, polytype, and method of formation. The measurements made on commercial, polycrystalline products should not be interpreted as being representative of single-crystal silicon carbide. The pressureless-sintered silicon carbides, being essentially single-phase, fine-grained, and polycrystalline, have properties distinct from both single crystals and direct-bonded silicon carbide refractories. Table 1 lists the properties of the fully compacted, high purity material.

Table 1. Properties of Silicon Carbide

Property	Value		References
mol wt	40.10		
decomposition temperature[a], °C			
α-form	2825 ± 40		7
β-form	2985		
sp gr, g/mL at 20°C			
β-form	3.210		
6H polytype[b]	3.211 (3.208)		
commercial	3.16		
refractive index			
β-form	2.48		8
α-form[b]	ε	ω	4
4H	2.712	2.659	
6H	2.690	2.647	
15R	2.687	2.650	
free energy of formation, $\Delta G°_f$, kJ/mol[c]			
α-form	504.1		9
β-form	506.2		
heat of formation, $\Delta H°_{f,298}$, kJ/mol[c]			
α-form	25.73 ± 0.63		
β-form	28.03 ± 2		
thermal conductivity at 25°C, W/(m·K)			11
commercial, high density	125.6		
reaction bonded	129.7		
emissivity[d]			11–16
spectra (3–5 μm)	0.9		
total (0–1600°C)	0.9		
coefficient of thermal expansion[d], per °C			16–22
25–200°C	2.97×10^{-6}		
25–600°C	4.27×10^{-6}		
700–1500°C	6.08×10^{-6}		
Young's modulus, GPa[e]			23,24
α-form, hot-pressed	440		
α-form, sintered	410		25
β-form, sintered	410		23,24
shear modulus, GPa[e]			
reaction-bonded	167.3		26
α-form, sintered	177		27
β-form, sintered	140–190		23

sublimed	19	28

[a] The decomposition products are Si, Si_2C, Si_2, SiC, and Si_3.

[b] H hexagonal, R rhombohedral.

[c] To convert J to cal, divide by 4.184.

[d] Of the sintered α-form.

[e] To convert GPa to psi, multiply by 145,000.

Silicon carbide is well known as a hard material occupying a relative position on Mohs' scale between alumina at 9 and diamond at 10 (see HARDNESS). The average values for Knoop hardness under a load of 100 g are

Material	Knoop hardness
sapphire *[1317-82-4]*	2013
SiC, dense, direct-bonded	2740
SiC, sintered alpha	2800
SiC, black single crystal	2839
SiC, green single crystal	2875
boron carbide	3491

Because of high thermal conductivity and low thermal expansion, silicon carbide is very resistant to thermal shock as compared to other refractory materials.

Crystal Structure. Silicon carbide may crystallize in the cubic, hexagonal, or rhombohedral structure. There is a broad temperature range where these structures may form. The hexagonal and rhombohedral structure designated as the α-form (noncubic) may crystallize in a large number of polytypes.

There are three possible arrangements of atoms in a layer of SiC crystal, and each type has the same layers but a different stacking sequence (29). Designation (30) is by the number of layers in the sequence, followed by H, R, or C to indicate whether the type belongs to the hexagonal, rhombohedral, or cubic class.

A number of theories have been put forth to explain the mechanism of polytype formation (30–36), such as the generation of steps by screw dislocations on single-crystal surfaces that could account for the large number of polytypes formed (30,35,36). The growth of crystals via the vapor phase is believed to occur by surface nucleation and ledge movement by face specific reactions (37). The solid-state transformation from one polytype to another is believed to occur by a layer-displacement mechanism (38) caused by nucleation and expansion of stacking faults in close-packed double layers of Si and C.

A progressive etching technique (39,40), combined with x-ray diffraction analysis, revealed the presence of a number of α polytypes within a single crystal of silicon carbide. Work using lattice imaging techniques via transmission electron microscopy has shown that α-silicon carbide formed by transformation from the β-phase (cubic) can consist of a number of the α polytypes in a syntactic array (41).

A phase diagram for the carbon–silicon system and for the relationship between temperature and solubility of carbon in silicon has been determined (42).

Mechanical Properties. Silicon carbide is a leading candidate material for rotating and static components in many gas turbine engine applications. As is the case for other ceramics, silicon carbide is brittle in nature. It is characterized by low fracture toughness and limited strain-to-failure as compared to metals. The strength of a silicon carbide component is determined by preexisting flaws introduced into the material during processing. The type, size, shape, and location of the flaws vary considerably and, consequently, so does the strength. Therefore designing with silicon carbide and other ceramics requires a probabilistic treatment of strength and component life (see FRACTURE MECHANICS). The strength, a statistical entity, can be described by the specification of at least two parameters, σ_0, the characteristic strength, and *m*, the Weibull modulus. These parameters are most commonly obtained from flexural strength data.

Sintered silicon carbide retains its strength at elevated temperatures and shows excellent time-dependent properties such as creep and slow crack growth resistance. Reaction-bonded SiC, because of the presence of free silicon in its microstructure, exhibits slightly inferior elevated temperature properties as compared to sintered silicon carbide. Table 2 (11,43) and Table 3 (44) show selected mechanical properties of silicon carbide at room and elevated temperatures.

Table 2. Flexure Strength and Fracture Toughness

Materialtype	Young's modulus,GPa[a]		Fracturetoughness,MPa·m$^{1/2}$[b]	Flexural strength,MPa[a,c]	
	20°C	1400°C		20°C	1400°C
hot-pressed SiC	440	380	3.9	650	500
range	430–450		3–4	300–800	175–575
sintered SiC	410	372	4.6	460	460
range	375–420	300–400	3.5–5.5	345–485	345–485
reaction-bonded SiC	380	275	4.9	310	190
range	360–400	200–320	3.5–6	175–450	70–450

[a] To convert Pa to psi, multiply by 1.45×10^{-4}.

[b] For a single-edged notched beam (SENB) test.

[c] Corresponding to a 4 pt. bend.

Table 3. Steady-State Creep for Alpha-Silicon Carbides

Density,g/mL	Temperature,K	Stress,MPa[a]	Creep rate,s^{-1}	Deformation,μm	Test duration,10^3 s
3.155	1820	138	1.06×10^{-9}	4.5	492.7
	1820	207	1.73×10^{-9}	6.0	356.2
	1820	276	2.23×10^{-9}	7.2	349.1
	1820	345	4.14×10^{-9}	7.7	271.9
	1820	414	5.10×10^{-9}	10.0	253.3
3.151	1923	69	[b]	6.5	360.5

	1923	138	6.37×10^{9}	15.0	260.4
	1923	207	1.02×10^{8}	27.0	319.3
	1923	276	1.68×10^{8}	23.7	175.1
	1923	345	2.25×10^{8}	34.0	181.7
	1923	414	3.18×10^{8}	62.0	238.4
3.160	2020	69	2.75×10^{8}	66.9	263.3
	2020	138	8.91×10^{8}	105.9	152.2
	2020	207	1.16×10^{7}	122.7	99.7
	2020	276	2.96×10^{7}	51.6	31.2
	2020	345	3.90×10^{7}	127.3	45.0
	2020	414	6.33×10^{7}	117.0	26.0
3.152	1823	179	[b]	14.5	117.4
	1873	179	6.55×10^{9}	19.5	378.2
	1923	179	1.46×10^{8}	70.0	356.3
	1973	179	5.56×10^{8}	64.0	161.5
	2023	179	2.00×10^{7}	128.0	89.3
	2073	179	6.33×10^{7}	47.0	14.8
3.153	1670	345	[b]	2.0	163.7
	1720	345	1.50×10^{9}	4.5	255.5
	1770	345	1.88×10^{9}	7.0	340.2
	1820	345	3.82×10^{9}	18.0	433.9
	1870	345	1.29×10^{8}	38.0	333.9
	1920	345	2.83×10^{8}	43.0	181.9
	1970	345	1.19×10^{7}	131.0	147.7
	2020	345	3.85×10^{7}	113.0	39.8
3.162	1670	414	3.68×10^{10}	2.0	492.4
	1720	414	9.75×10^{10}	4.2	351.4
	1770	414	2.52×10^{9}	8.6	346.8
	1820	414	5.09×10^{9}	16.0	325.9
	1870	414	1.14×10^{8}	25.0	354.8
	1920	414	3.11×10^{8}	67.0	264.1
	1970	414	1.28×10^{7}	160.4	165.4
	2020	414	5.34×10^{7}	143.7	36.0

[a] To convert MPa to psi, multiply by 145.

[b] Steady-state creep did not occur at these experimental conditions.

Electrical Properties. The electrical properties of silicon carbide are highly sensitive to purity, density, and even to the electrical and thermal history of the sample.

Resistivity. The temperature coefficient of electrical resistivity of commercial silicon carbide at room temperature is negative. No data are given for refractory materials because resistivity is greatly influenced by the manufacturing method and the amount and type of bond. Manufacturers should be consulted for specific product information.

The resistivity of heating elements made from recrystallized silicon carbide varies with raw material grain size, purity, porosity, etc. Typical resistivity is 0.1 ohm·cm at room temperature. Resistivity decreases with rising temperature to a minimum at 400°C and then gradually increases to about 0.13 ohm·cm at 1500°C. This has the effect of reducing the total power input used to heat a furnace up to temperature while preventing the heating element from overheating after the operating temperature has been reached. This resistivity–temperature characteristic is also beneficial in other devices such as gas igniters.

Resistivity measurements of doped, alpha-silicon carbide single crystals from 195 to 725°C showed a negative coefficient of resistivity below room temperature, which gradually changed to positive above room temperature (45). The temperature at which the changeover occurred increased as the ionization of the donor impurity increased. This is believed to be caused by a change in conduction mechanism.

Semiconducting Properties. Silicon carbide is a semiconductor: it has a conductivity between that of metals and insulators or dielectrics (4,13,46,47). Because of the thermal stability of its electronic structure, silicon carbide has been studied for uses at high (>500°C) temperature. The Hall mobility in silicon carbide is a function of polytype (48,49), temperature (41,42,45–50), impurity, and concentration (49). In *n*-type crystals, activation energy for ionization of nitrogen impurity varies with polytype (50,51).

Resistivity is strongly dependent on crystal structure and impurities. It is generally accepted that boron and nitrogen can substitute for carbon in the SiC lattice (52,53) and aluminum is thought to substitute for silicon (49). Silicon carbides having resistivities as high as 10^{11} ohm·cm have been prepared (54). These have potential for use as semiconductor substrates, because the SiC has higher thermal conductivity than alumina, allowing better thermal dissipation (54) (see SEMICONDUCTORS).

Optical absorption measurements give band-gap data for cubic silicon carbide as 2.2 *e*V and for the α-form as 2.86 *e*V at 300 K (55). In the region of low absorption coefficients, optical transitions are indirect whereas direct transitions predominate for quantum energies above 6 *e*V. The electron affinity is about 4 *e*V. The electronic bonding in silicon carbide is considered to be predominantly covalent in nature, but with some ionic character (55). In a Raman scattering study of valley-orbit transitions in 6H-silicon carbide, three electron transitions were observed, one for each of the inequivalent nitrogen donor sites in the silicon carbide lattice (56). The donor ionization energy for the three sites had values of 0.105, 0.140, and 0.143 *e*V (57).

Radiation Effects. Alpha silicon carbide exhibits a small degree of anisotropy in radiation-induced expansions along the optical axis and perpendicular to it (58). When diodes of silicon carbide were compared with silicon diodes in exposure to irradiation with fast neutrons (59), an increase in forward resistance was noted only at a flux about 10 times that at which the increase occurs in a silicon diode. In general, it appears that silicon carbide, having the more tightly bound lattice, is less damaged by radiation than silicon.

Reactions

Silicon carbide is comparatively stable. The only violent reaction occurs when SiC is heated with a mixture of potassium dichromate and lead chromate. Chemical reactions do, however, take place between silicon carbide and a variety of compounds at relatively high temperatures. Sodium silicate attacks SiC above 1300°C, and SiC reacts with calcium and magnesium oxides above 1000°C and with copper oxide at 800°C to form the metal silicide. Silicon carbide decomposes in fused alkalies such as potassium chromate or sodium chromate and in fused borax or cryolite, and reacts with carbon dioxide, hydrogen, air, and steam. Silicon carbide, resistant to chlorine below 700°C, reacts to form carbon and silicon tetrachloride at high temperature. SiC dissociates in molten iron and the silicon reacts with oxides present in the melt, a reaction of use in the metallurgy of iron and steel (qv). The dense, self-bonded type of SiC has good resistance to aluminum up to about 800°C, to bismuth and zinc at 600°C, and to tin up to 400°C; a new silicon nitride-bonded type exhibits improved resistance to cryolite.

In a study of oxidation resistance over the range 1200–1500°C an activation energy of 276 kJ mol (66 kcal mol) was determined (60). The rate law is of the form $\delta^2 \quad kT + C$; the rate-controlling step is probably the diffusion of oxygen inward to the $SiC–SiO_2$ interface while CO diffuses outwards.

The oxidation rate of granular silicon carbide in dry oxygen at 900–1600°C was studied and an equation for the effect of particle size was derived (61). Small changes in impurity content did not affect this rate but the presence of water vapor and changes in partial pressure of oxygen were critical (61,62). Steam and various impurities and binders also affect the oxidation of silicon carbide (63). Differences have been observed in oxygen adsorption on the different SiC crystal faces (64).

At high temperature, silicon carbide exhibits either active or passive oxidation behavior depending on the ambient oxygen potential (65,66). When the partial pressure of oxygen is high, passive oxidation occurs and a protective layer of SiO_2 is formed on the surface.

$$2SiC(s) + 3O_2(g) \rightarrow 2SiO_2(s) + 2CO(g)$$

Active oxidation occurs where the oxygen partial pressure is low and gaseous oxidation products are formed.

$$SiC(s) + O_2(g) \rightarrow SiO(g) + CO(g)$$

$$SiC(s) + 2SiO_2(s) \rightarrow 3SiO(g) + CO(g)$$

A fresh surface of silicon carbide is thus constantly being exposed to the oxidizing atmosphere. Active oxidation takes place at and below approximately 30 Pa (0.23 mm Hg) oxygen pressure at 1400°C (66). Passive oxidation is determined primarily by the nature and concentration of impurities (67).

Manufacture and Processing

Powder Preparation. There are several routes to preparing SiC powders having variable purity levels, crystal structure, particle size, shape, and distribution. Methods that have been examined include growth by sublimation from the vapor phase, carbothermic reduction, and crystallization from a melt.

Carbothermic Reduction. Silicon carbide is commercially produced by the electrochemical reaction of high grade silica sand (quartz) and carbon in an electric resistance furnace. The carbon is in the form of petroleum coke or anthracite coal. The overall reaction is

$$SiO_2 + 3C \rightarrow SiC + 2CO(g)$$

Sawdust may be added to increase the porosity of the furnace charge, thus increasing the circulation of the reacting gases and facilitating the removal of CO. The process has been reviewed (68). The substitution of anthracite coal for coke was advocated in the 1950s (69). In many instances chlorine gas can be introduced into the reaction zone to remove impurities (70). Also, addition of small amounts of boron, titanium, or zircon to the furnace charge reduces the product sensitivity to oxidation at 900–1100°C (71). In the Acheson process described above, the reduction of silica is carried out at temperatures in excess of 2100°C resulting in α-SiC grains. The product produces crystals with a color that varies from pale yellow or green to black, depending on the amount of impurities. The manufactured product is usually crushed and graded for size.

The carbothermic reduction can also be carried out at lower (about 1500°C–1600°C) temperature resulting in β-SiC formation (72).

Polymer Conversion. The polymer conversion method consists of heating an organosilicon polymer, thereby obtaining a skeleton that contains carbon and silicon, to produce silicon carbide (73–77). Polycarbosilanes and polyborosiloxanes have been used. Some of the precursors for the organic polymer are polydimethylsilane obtained by a dechlorination condensation reaction of dimethyldichlorosilane *[75-78-5]*, $C_2H_6Cl_2Si$. In many of these conversions, complete SiC formation is never achieved and beta silicon carbide coexists with graphite microcrystals. The material also has high (>10 wt%) oxygen content and hydrogen (0.02–8 wt %) content. Of the various thermal decomposition products of organosilicon polymers, the β-SiC ultrafine powder from polyborosiloxane was found to have the best sinterability. Polymer conversion routes have been quite successful in fabricating high strength SiC fiber such as Nicalon fiber.

Gas-Phase Synthesis. A gas-phase synthesis route to making fine, pure SiC having controllable properties has been described (78,79). Methane was used as a carbon source if required, and the plasma decomposition of three feedstocks, silicon tetrachloride *[10026-04-7]*, $SiCl_4$, dimethyldichlorosilane, and methyltrichlorosilane *[75-79-6]*, CH_3Cl_3Si, into fine SiC powders was investigated.

Another method of manufacturing SiC by the decomposition of a gas mixture containing silane, propane, and hydrogen, and hydrogen chloride has been described (80). With such a mixture, it was possible to work at a relatively lower (1200°C) temperature and it was claimed that compact, homogeneous β-SiC crystals were obtained. In a variation of this gas-phase synthesis theme, SiC has been produced from the reaction of $SiCl_4$ and methane (81). SiC precipitates from 1000 to 3000°C.

Monolithic Sintered Silicon Carbide. In 1973, it was demonstrated that the simultaneous presence of boron and carbon is required to densify, without pressure, a green compacted body of beta silicon carbide (82). Pressureless sintering techniques were subsequently established (83–86) for α-SiC powder made by inexpensive methods such as the Acheson process. In either case, a density above 98% theoretical is reported. The SiC powder used plays the most decisive role in obtaining high sintered densities and uniform microstructures. Essential characteristics are the kind and quantity of impurities, grain size, and the specific surface area (87,88). A densification mechanism by volume or grain boundary diffusion in the solid state has been reported for boron- and carbon-doped SiC (89–93). Various ceramic-forming methodologies such as dry pressing, slip casting, extrusion and injection molding, can be used to produce both simple and complex shapes using the pressureless sintering process.

This boron- and carbon-doped SiC exhibits excellent strength and stiffness, extreme hardness, and thermal and chemical resistance. The strength of this system is not affected by temperatures up to 1650°C. Creep is virtually nonexistent up to 1400°C. Cyclic durability testing conducted at 1370°C in air showed no deterioration of strength after 3500 h (94).

Pressureless sintering of α- and β-SiC powders can also be achieved by the addition of aluminum and or aluminum compounds together with carbon or rare-earth elements (95–105). Boron-free, aluminum-containing sintering aids inhibit grain growth (95,104). Aluminum oxide together with yttrium oxide as additives yield a fine and unique microstructure (104). A liquid-phase sintering mechanism has been reported in this aluminum oxide and rare-earth oxide-doped SiC system (104,106). Fine microstructure, good chipping resistance, and over 800 MPa (116,000 psi) room temperature strength have been reported (97,104). Creep resistance and other high temperature related properties are not as good as the boron- and carbon-doped SiC, in general.

Other types of sintering additives such as Be, P, N, and nitrogen compounds have been used (107–110) to modify the electrical properties of SiC, which is intrinsically a semiconductive material. Beryllium and its compounds increased the electrical resistivity dramatically, while maintaining good thermal conductivity, and provided a feasible route to make SiC substrates for electronic applications; however, the potential health hazard of beryllium compounds has become an issue. Nitrogen and P together with Al and B, on the other hand, reduce the electrical resistivity of SiC. This electrically conductive SiC and its good oxidation resistance make SiC an attractive material for heating element and igniter applications.

Reinforcements. The high modulus, high intrinsic strength, and temperature stability make SiC, in the form of whiskers, platelets, and fibers, a promising candidate reinforcement material for metal, polymer, and ceramic matrix composites (qv).

Silicon carbide whiskers are all grown from the gas phase in one fashion or another. Those grown at the relatively low temperatures of 1200 to 1800°C are composed of mostly β-SiC, those grown above 2000°C of α-SiC. Ribbonlike crystals are formed by sublimation (recrystallization) techniques similar to the Lely process. Hairlike crystals are mostly formed by a variety of chemical vapor deposition processes: from gaseous silicon–carbon compounds in the low temperature range, giving either α- or β-SiC; by reaction of gaseous carbon compounds with $SiCl_4$, usually at heated filaments such as *W* or on graphite surfaces, forming β-SiC; by reaction of hydrocarbons or other gaseous carbon species and silica at 1300 to 1500°C, for example, $3CH_4 + SiO_2 \rightarrow SiC + 2CO + 6H_2$.

The hydrocarbon is carried in a stream of H_2 or Ar, and β-SiC is formed; or β-SiC is formed by reaction in the gas phase, under static conditions, of compounds such as SiO or CO formed *in situ* during the process. In this latter case the important reaction appears to be $SiO + 3CO \rightarrow SiC + 2CO_2$. This

takes place in some regions of the commercial Acheson furnace and in the Lely-type furnace.

In all of these processes it is possible to increase the yield of whiskers by adding metallic impurities, and the sublimation process requires such additions. The vapor–liquid–solid (VLS) growth mechanism is often thought to be involved.

Silicon carbide whiskers typically have diameters of a few micrometers and lengths up to 5 cm. They may be composed of either β-SiC or α-SiC, the latter in one or more polytypes, and occur mostly as hair- or ribbonlike crystals. Despite many attempts to produce SiC whiskers on a large scale at low cost, they have never acquired a wide importance. SiC whiskers have been reviewed (111–120).

Silicon carbide is also a prime candidate material for high temperature fibers (qv). These fibers are produced by three main approaches: polymer pyrolysis, chemical vapor deposition (CVD), and sintering. Whereas fiber from the former two approaches are already available as commercial products, the sintered SiC fiber is still under development. Because of its relatively simple process, the sintered α-SiC fiber approach offers the potential of high performance and extreme temperature stability at a relatively low cost. A comparison of the manufacturing methods and properties of various SiC fibers is presented in Table 4 (121,122).

Table 4. SiC Fiber Manufacturing Methods and Properties[a]

Manufacturingmethod	Tradename	Manufacturer	Strength, GPa[b]	Maximum usetemperature, °C	Modulus, GPa[b]	Diameter, μm
sintering	[c]	Carborundum	0.93–1.24	>1550	414	30–100
		DuPont[d]	0.76	na	414	30–100
polymer pyrolysis	HPZ	Dow Corning	2.76	1300	193	10–12
	Nicalon	Nippon Carbon	2.62	1200	193	10
	Tyranno	Ube	2.76	1300	193	10
CVD coating	Sigma	BP Carborundum	3.45–4.14	1250	414	100
	SCS-6	Avco	3.45–4.14	1400	414	140

[a] Ref. 121.

[b] To convert GPa to psi, multiply by 145,000.

[c] Sintered SiC fibers are still experimental.

[d] Ref. 122.

Alpha-SiC can also be synthesized in the form of platelets, a form that is often preferred because it poses fewer health risks than whiskers and is easier to process. The platelets are bounded top and bottom by a basal plane. They are grown by reaction of carbon and silica at high temperatures or by recrystallization of β-SiC, the low temperature structure of SiC, to α-SiC (123,124). When the basal planes are deactivated, commonly by the presence of B or Al compounds, the platelet is forced to grow in the planes perpendicular to the basal plane (125–127). Aspect ratios, the ratio of maximum length to minimum dimension, of 10 or greater are possible by appropriate choice of shape control additives. Various grades have been marketed. Average maximum dimensions range from 15 μm to over 100 μm (128–130). The platelets are mostly single crystals with 6H structure, but mixed polytypes can occur within a single platelet. The single-crystal character and the highly stable structure lead to the maximum stability possible in a SiC reinforcement. Platelets are being used mostly in Al-based metal matrix composites (MMC) but have been studied as reinforcements for ceramics (qv) also.

Economic Aspects

Silicon carbide was first manufactured on a large scale in 1892, but production did not reach 8200 t yr until 1918. World production of silicon carbide was over 790,000 t yr in 1988 (Table 5). The average value per ton of all grades of SiC was $388.

Table 5. 1988 Annual World Capacity of Silicon Carbide

Region	Capacity, t
North America	
United States and Canada	126,600
Mexico	22,700
Total	*149,300*
South America	
Brazil	12,700
Europe	
France	16,300
Germany	36,300
Italy	36,300
The Netherlands	45,400
Norway	74,000
Spain	18,200
Total	*226,500*
Eastern Europe	
Czechoslovakia, Poland, Russia, Yugoslavia	158,900
Asia	
China	145,200
India	13,600
Japan	86,200
Total	*245,100*
World Total	*792,500*

Table 6 shows the production of abrasive silicon carbide in the United States and Canada (131). In 1988, four firms were producing crude silicon carbide under various trade names at six plants in the United States and Canada, The Exolon-ESK Co.; General Abrasive Dresser Co.; Norton Co.; and Superior Graphite Co. Most plants are located in areas where electrical power is, or at one time, was available at relatively low rates. Other considerations are availability of labor, reasonable air and water pollution standards, future expansion potential, and proximity of raw materials and markets.

One of the first important uses of silicon carbide was as an abrasive (see ABRASIVES). Additional markets in refractories, electrical devices, and metallurgy have since been developed. In 1988, the silicon carbide market was estimated at 55% metallurgical, 43% abrasive, and 2% for refractories and

other uses in terms of production. In terms of value, the proportions were 50% , 47% , and 3% , respectively, for metallurgical uses, abrasives, and refractories and other uses.

Table 6. Silicon Carbide Production in the United States and Canada

Year	Quantityproduced, t	Value,$ × 10^3
1984	124	57,125
1985	103	42,563
1986	113	48,064
1987	113	48,790
1988	118	50,559

Specifications and Standards

In the United States the test methods, specifications, and standards for abrasive grain products are established by the Abrasive Grain Association (AGA) (132), the Grinding Wheel Institute (GWI) (133), and the Coated Abrasive Manufacturing Institute (CAMI) (134). These associations publish standards and specifications through the American National Standard Institute, Inc. (ANSI), New York. In Europe, the International Standards Organization (ISO) issues standards in cooperation with corresponding associations in Austria, France, Germany, Great Britain, Italy, Norway, Spain, Sweden, and Switzerland. The Japanese Standards Association (135) issues standards and methods for Japan. In addition, principal silicon carbide producers have tests, processes, and product specifications for internal use, usually for products not covered by industry standards.

Analytical and Test Methods

The analysis of silicon carbide involves identification, chemical analysis, and physical testing. For identification, x-ray diffraction, optical microscopy, and electron microscopy are used (136). Refinement of x-ray data by Rietveld analysis allows more precise determination of polytype levels (137).

Chemical analysis of abrasive grain and crude in the United States is carried out by using a standard analysis scheme approved by the AGA (132) and issued by the ANSI (138). Grain is usually analyzed for silicon carbide content, free silicon, free carbon, free silica, calcium oxide, magnesium oxide, and oxides of iron, titanium, and aluminum. The standard scheme specified by ANSI uses a combination of gravimetric, volumetric, calorimetric, and atomic absorption techniques. Carbon is usually converted by combustion to carbon dioxide, which is then measured by weighing an absorption bulb (138) or by reading the electrical or thermal conductivity (139). A silicon carbide standard reference material, NBS SRM-112b, is available (140). In Europe and Japan, standard analysis schemes, similar to the ANSI scheme, have been developed by ISO (141) and JSA (142). Instrumental techniques such as x-ray fluorescence, emission spectroscopy, atomic absorption, and neutron activation analysis are used as additional methods of analysis, especially where applications require knowledge of a wide range of trace metals.

In the United States, a number of physical tests are performed on silicon carbide using standard AGA-approved methods, including particle size (sieve) analysis, bulk density, capillarity (wettability), friability, and sedimentation. Specifications for particle size depend on the use; for example, coated abrasive requirements (134) are different from the requirements for general industrial abrasives. In Europe and Japan, requirements are again set by ISO and JSA, respectively. Standards for industrial grain are approximately the same as in the United States, but sizing standards are different for both coated abrasives and powders.

Toxicity

Silicon carbide has been described as a mild inhalation irritant (143). The threshold limit value for silicon carbide in the atmosphere is 5 mg/m^3. Because of increased interest in SiC whiskers as a reinforcement for composites, the ASTM has established Subcommittee E34.70 on Single-Crystal Ceramic Whiskers to write standards for handling this form of SiC (144).

Uses

Wear Surfaces. The extreme hardness of silicon carbide leads to its use where wear resistance is important as in brake linings (see BRAKE LININGS AND CLUTCH FACINGS) or electrical contacts, and for nonslip applications such as floor or stair treads, terrazzo tile, deck-paint formulations, and in road surfaces. SiC is commonly used as a seal face material in mechanical seals used in pumps, compressors, and agitators in a wide variety of demanding environments including highly corrosive ones. More recent applications include the use of silicon carbide in automotive water pump seals and faucet washers. Other uses include blast and atomization nozzles, rocket nozzle inserts, thrust and journal bearings in magnetically driven pumps, pump sleeves, valve seats, and choke inserts.

Armor. Silicon carbide is used as a candidate in composite armor protection systems. Its high hardness, compressive strength, and elastic modulus provide superior ballistic capability to defeat high velocity projectile threats. In addition, its low specific density makes it suitable for applications where weight requirements are critical (11).

High Temperature. The low coefficient of thermal expansion and high thermal conductivity of silicon carbide bestow it with excellent thermal shock resistance. Combined with its outstanding corrosion resistance, it is used in heat-transfer components such as recuperator tubes, and furnace components such as thermocouple protection tubes, crucibles, and burner components. Silicon carbide is being used for prototype automotive gas turbine engine components such as transition ducts, combustor baffles, and pilot combustor support (145). It is also being used in the fabrication of rotors, vanes, vortex, and combustor.

Refractories. Its low coefficient of expansion, high thermal conductivity, and general chemical and physical stability make silicon carbide a valuable material for refractory use. Suitable applications for silicon carbide refractory shapes include boiler furnace walls, checker bricks, mufflers, kiln furniture, furnace skid rails, trays for zinc purification plants, etc (see REFRACTORIES).

Electrical. Heating elements made from recrystallized silicon carbide, used in electric furnaces, operate up to about 1600°C and represent a significant electrical use of silicon carbide. Heating elements are also used as a source of infrared radiation for drying operations, a light source for mineral determinations, and an ignition source for oil- or gas-fired burners. A more recent use is in ignition devices for gas clothes dryers and cooking ranges.

The semiconducting properties of silicon carbide have led to its use in thermistors (temperature-sensitive devices) and in varistors (voltage-sensitive devices). Thermistors are used for measuring and controlling temperature, as compensating devices for induction coils in electronic circuitry, and for time-delay applications. Varistors protect the coils or contacts in relays and solenoids against high voltage surges, limit the inductive kick in oil burner ignition circuits, and stabilize circuits supplied by rectifiers.

A high temperature thermocouple uses silicon carbide (146). It is also used in lightning arrestors to protect high tension power lines, and in high loss factor microwave attenuators (147).

Considerable interest in the solid-state physics of silicon carbide, that is, the relation between its semiconductor characteristics and crystal growth, has resulted from the expectation that SiC would be useful as a high temperature-resistant semiconductor in devices such as point-contact diodes (148), rectifiers (149), and transistors (150,151) for use at temperatures above those where silicon or germanium metals fail (see SEMICONDUCTORS).

Other solid-state applications of silicon carbide include its use as an electroluminescent diode for use in sound recording equipment and photomultipliers and controllers. It has been studied as a reflective surface for lasers. By combining its excellent thermal conductivity and high electrical resistance, silicon carbide has also found application as an insulating material for integrated circuit substrates.

Abrasives. Silicon carbide is used in loose form for lapping; mixed with a vehicle to form abrasive pastes or sticks; mixed with organic or inorganic binders; shaped and cured to form abrasive wheels, rubs, or tumbling nuggets; bonded to paper or cloth backings to form abrasive sheets, disks, or belts; or incorporated with the fibrous backing material before sheeting. Silicon carbide is harder yet more brittle than abrasives (qv) such as aluminum oxide. Because the grains fracture readily and maintain a sharp cutting action, silicon carbide abrasives are generally used for grinding hard, low tensile-strength materials such as chilled iron, marble, and granite, and materials that need sharp cutting action such as fiber, rubber, leather, or copper.

Metallurgy. Silicon carbide is used extensively in ferrous metallurgy. When added to molten iron, a vigorous exothermic reaction takes place decomposing the silicon carbide and resulting in a hotter melt. The effect is to deoxidize and cleanse the metal and promote fluidity. Thus a more desirable random distribution of the graphite flakes is achieved and a more machinable product obtained. Present practice is to add the silicon carbide as briquettes to the cupola or in loose granular form to induction furnaces when producing cast iron (see IRON). When added as granules to molten steel in the ladle, it reduces the number of undesirable inclusions and leads to better physical properties in the product. When added as granules to steel in a basic oxygen furnace it extends the capacity of the furnace to melt more scrap as a result of the exothermic reaction.

Other Uses. The special characteristics of silicon carbide give rise to a wide range of applications, including catalyst-carrier nuggets, tower packing, and pebbles for pebble-bed heaters or fluidized-bed reactors. It is used as a raw material for the production of silicon tetrachloride; in welding-rod compositions; as a filler in elastomers (see FILLERS); as an additive in other ceramic materials to increase high temperature resistance; and as an ingredient of red glaze (see CERAMICS). Silicon carbide has been tested as a diluting agent in the coal gasification process (see COAL CONVERSION PROCESSES).

The ultrafine silicon carbide produced in an electric arc is used as an insulation in cryogenic applications (152) (see CRYOGENICS). It generally increases the wear resistance of the paint film when added to paint formulations.

Coatings of dense silicon carbide have been applied to materials such as graphite or silicon by various chemical vapor deposition processes. The coatings increase the oxidation and erosion resistance of the substrates for a wide range of applications. A silicon carbide–graphite material has been developed by Carborundum that can serve as a sputtering coating target.

Silicon carbide's relatively low neutron cross section and good resistance to radiation damage make it useful in some of its new forms in nuclear reactors (qv). Silicon carbide temperature-sensing devices and structural shapes fabricated from the new dense types are expected to have increased stability. Silicon carbide coatings (qv) may be applied to nuclear fuel elements, especially those of pebble-bed reactors, or silicon carbide may be incorporated as a matrix in these elements (153,154).

A silicon carbide-bonded graphite material in which graphite particles are distributed through the silicon carbide matrix has high thermal shock resistance and is suitable for applications including rocket nose cones and nozzles and other severe thermal shock environments (155) (see ABLATIVE MATERIALS).

Materials made of silicon nitride, silicon oxynitride, or sialon-bonded silicon carbide have high thermal shock and corrosion resistance and may be used for pump parts, acid spray nozzles, and in aluminum reduction cells (156–159). A very porous silicon carbide foam has been considered for surface combustion burner plates and filter media. It can also be used as a substrate carrying materials such as boron nitride as planar diffusion source for semiconductor doping applications.

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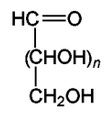
CARBOHYDRATES

Carbohydrates are found in all plant and animal cells. They are the most abundant of the organic compounds, so abundant that it is estimated that well over half of the organic carbon on earth exists in the form of carbohydrates. Most carbohydrates are produced and found in plants. Carbohydrate molecules make up about three-fourths of the dry weight of plants; most of this is found in cell walls as structural components. Carbohydrates also constitute important energy reserves in plants; one carbohydrate, starch, provides about three-fourths of the calories in the average human diet on a worldwide basis. But the nutritional aspects are only a part of the story of carbohydrates. They have many important industrial uses in such diverse areas as the adhesive, agricultural chemicals, fermentation, food, paper and related products, petroleum production, pharmaceutical, and textile industries. Because the basic carbohydrate molecule is functionalized at every carbon atom, and because carbohydrates seldom occur as simple sugars but rather combined with each other or other compounds, the variety of carbohydrates in nature is large, and the number of theoretical possibilities is essentially limitless.

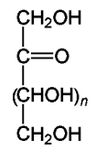
Classification

The basic carbohydrate molecule possesses an aldehyde or ketone group and a hydroxyl group on every carbon atom except the one involved in the carbonyl group. As a result, carbohydrates are defined as aldehyde or ketone derivatives of polyhydroxy alcohols and their reaction products. A look at the formula for glucose ($C_6H_{12}O_6$) shows that it contains hydrogen and oxygen atoms in the ratio in which they are found in water. The name carbohydrate (hydrate of carbon) is derived from the fact that the basic carbohydrate molecule has the formula $C_n(H_2O)_n$.

In common practice, all low molecular weight carbohydrates are called sugars. Monosaccharides, commonly referred to as the simple sugars, are carbohydrates that cannot be broken down by hydrolysis (1). They are classified both according to the kind of carbonyl group and according to the number of carbon atoms contained in the molecule. An aldose is a polyhydroxy aldehyde, ie, an aldehyde that has a hydroxyl group on every carbon atom except the carbonyl carbon atom. A ketose is a polyhydroxy ketone. The two classification systems can be joined in a single-word description. For example, a three-carbon aldose is an aldotriose and a six-carbon ketose is a ketohexose.



aldose



ketose

Numical prefixes designating the number of carbon atoms are tri-, tetr-, pent-, hex-, hept-, etc. In systemic nomenclature, the suffix for the names of aldehyde sugars is -ose and for ketone sugars -ulose. However, common names are commonly used, creating exceptions in both cases. Systematic generic terms for aldoses and ketoses are glycose and glycosulose, respectively.

Monosaccharides are most often joined together in chains. Oligosaccharides are carbohydrate chains that yield 2–10 monosaccharide molecules upon hydrolysis (2–4). Oligosaccharides are classified according to the number of monosaccharide units in them, eg, di-, tri-, tetra-, pentasaccharides, etc. Polysaccharides are carbohydrate chains that yield at least 35 monosaccharide molecules upon hydrolysis (2,5–9). Polysaccharides may be linear (unbranched) or branched. They may contain a single kind of monosaccharide unit (homopolysaccharides) or two or more different monosaccharide units (heteropolysaccharides). The generic term for polysaccharides is glycan; therefore, these two groups of polysaccharides may also be termed homoglycans and heteroglycans.

Most carbohydrates exist in the form of polysaccharides. Polysaccharides give structure to the cell walls of land plants (cellulose), seaweeds, and some microorganisms and store energy (starch in plants and glycogen in animals). They are important in the human diet and in many commercial applications.

Representations.

D-Glucose is an aldohexose. Four of the six carbon atoms are chiral carbon atoms. To compare the arrangements of atoms in common, simple monosaccharides, structural formulas are written using the convention that all bonds connecting carbon atoms are vertical and project into the plane of the page away from the viewer and the bond to the hydrogen atom and the hydroxyl group on each chiral carbon atom projects out of the plane of the page towards the viewer. Horizontal bonds are often omitted. The acyclic structural formula of D-glucose shown is known as the open-chain, or Fischer, formula. If the hydroxyl group on the most distant chiral carbon atom from the top end (the penultimate carbon atom of the structures in Figure 1; C-5 of D-glucose) is on the right when the carbon chain of an aldose or ketose is written using this convention, the sugar is said to have the D configuration; if that hydroxyl group is on the left, the sugar belongs to the family of L sugars. Most naturally occurring monosaccharides have the D configuration. An exception is arabinose, which most often occurs as L-arabinose *[5328-37-0]*. All possible structures of the three-, four-, five-, and six-carbon-atom aldoses with the D configuration are given in Figure 1.

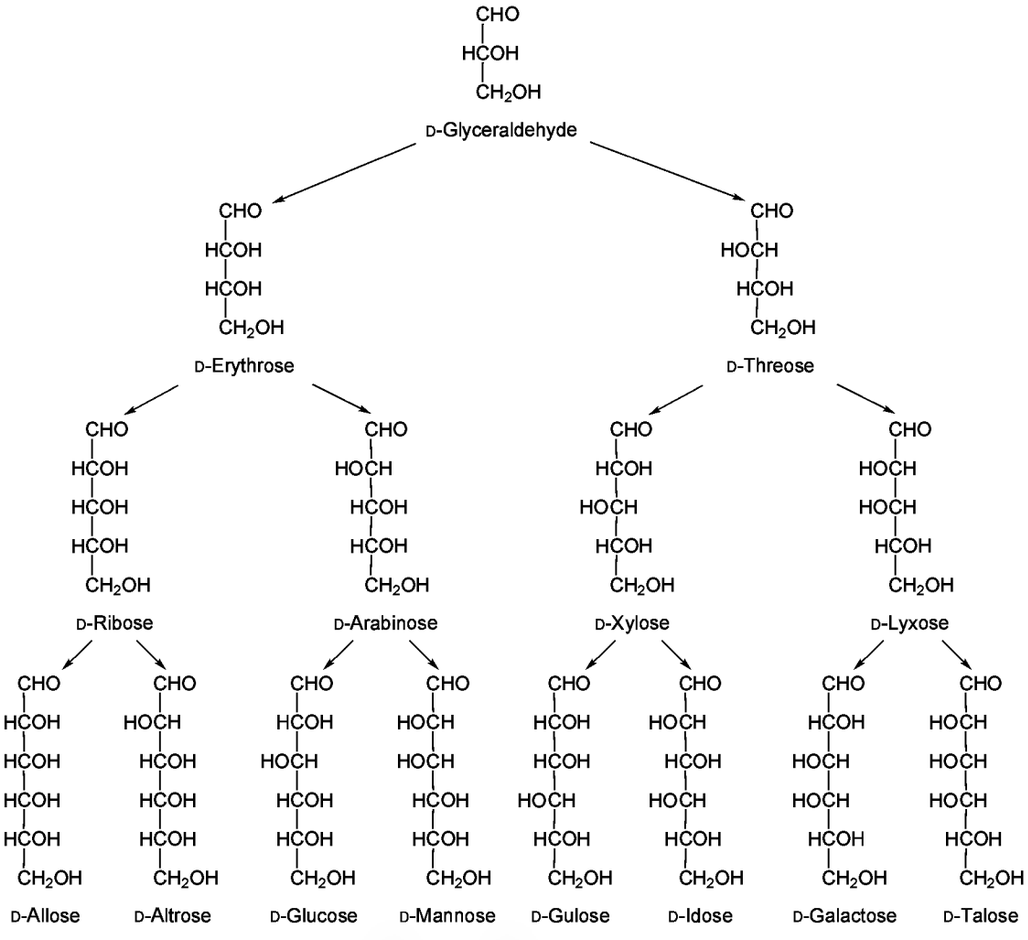


Fig. 1. The family of D-aldoses derive from D-glyceraldehyde by chain extension at the carbonyl carbon atom.

Because a hexose contains four chiral carbon atoms, there are 2^4 16 different possible arrangements of the hydroxyl groups in space, ie, there are 16 different stereoisomers. The structures of half of these, the eight D isomers, are shown in Figure 1. Only three of these 16 stereoisomers are commonly found in nature: D-glucose *[50-99-7]*, D-galactose *[59-23-4]*, and D-mannose *[3458-28-4]*.

Chemistry of Saccharides

Most carbohydrates have two kinds of reactive groups: the carbonyl group and primary and secondary hydroxyl groups.

REACTIONS OF THE CARBONYL GROUP

Ring Forms. Aldehydes and ketones react with compounds containing a hydroxyl group (alcohols) to form first hemiacetals and then acetals. Because aldose and ketose molecules have a carbonyl group and hydroxyl groups on the same carbon chain, they can form hemiacetals intramolecularly, as well as by reacting with another molecule. Such an intramolecular reaction forms a ring. The most common rings are the six-membered pyranose ring, a cyclic structure composed of five carbon atoms and one oxygen atom, and the five-membered furanose ring, a cyclic structure composed of four carbon atoms and one oxygen atom (Fig. 2) (1).

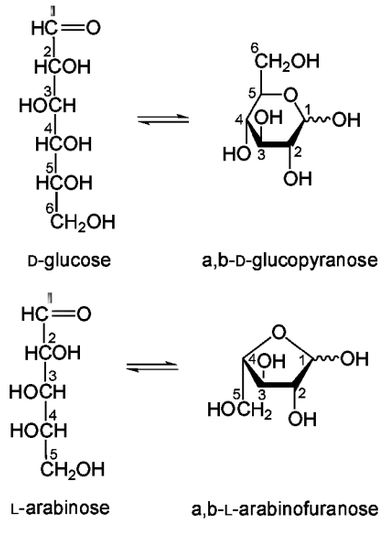


Fig. 2. Conversion from open-chain to ring forms of aldosugars. When ring closure occurs, a new chiral center is formed and two C-1 configurational isomers, called anomers, are formed.

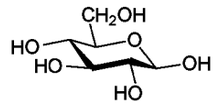
It is easy to picture the formation of a ring from an open-chain structure if it is remembered that the carbon chain is curving into the plane of the

page. When, this structure is laid on its side, it is naturally curved into almost the correct shape, with the ends almost touching. However, in order to close the ring, ie, to form the hemiacetal between the hydroxyl group on C-5 and the aldehyde group, C-5 must rotate to bring the hydroxyl group closer to the aldehyde group. The result of this rotation is that the $-CH_2OH$ group sticks up in this (the Haworth) representation of the pyranose ring of the D sugars and the $-CH_2OH$ group projects down in representations of the L sugars. Most, but not all, naturally occurring sugars are D sugars. For C-2, C-3, and C-4, the carbon atoms that are not involved in ring formation, the hydroxyl groups that are on the right in the Fischer projection project down in the Haworth ring form and the hydroxyl groups that are on the left in the Fischer projection stick up in the Haworth ring form.

When the pyranose (six-membered) ring is formed, a new chiral carbon atom is formed from C-1. Thus there can be two forms of the pyranose ring. D Sugars with the hydroxyl group at C-1 in the up position are said to be in the beta (β) configuration; D sugars with the hydroxyl group at C-1 projecting down are said to be in the alpha (α) configuration. α-D-Glucopyranose *[492-62-6]* and β-D-glucopyranose *[492-61-5]* are anomers of each other. In β-L-pyranoses, the hydroxyl group on C-1, termed the anomeric carbon atom, projects down in the Haworth representation. Thus, for example, β-D- and β-L-glucopyranose *[39281-65-7]* are complete mirror images of each other.

Most free pentoses, hexoses, and heptoses occur primarily in less strained pyranose rings, but the furanose ring is also quite important. The furanose ring is formed in the same way as the pyranose ring and also occurs in α and β forms. This is demonstrated with L-arabinose, which is commonly found in polysaccharides in the form of α-L-arabinofuranosyl units (see Fig. 2).

Whereas furanose rings are almost, but not quite, flat, pyranose rings are not, thus Haworth representations do not show the actual molecular shape. Pyranose rings assume one of two chair forms designated the $^4C_1$ chair because C-4 is up and C-1 is down or the $^1C_4$ form. The $^4C_1$ chair is by far the most prevalent shape of the β-D-glucopyranose molecule because all the bulky groups (the hydroxyl groups at C-1, C-2, C-3, and C-4 and the hydroxymethyl group at C-5) are in equatorial positions which minimizes nonbonded (steric) interactions (1).



Solutions of all carbohydrates containing a saccharose group reach an equilibrium between various forms, as shown for D-glucose in Figure 3. The exact composition of an equilibrium mixture depends on the temperature and the specific sugar; for D-glucose the approximate composition of a solution at room temperature is <0.01% aldehydo form, 36.2% α-D-glucopyranose, 63.8% β-D-glucopyranose, and traces of the furanose ring forms. The process of conversion between forms is called mutarotation (1) because, when crystals of α-D-glucopyranose are dissolved in water, the initial specific optical rotation ($[\alpha]_D$ at 20°C) of +112° gradually decreases to the equilibrium value of +52.7°. Likewise, when crystals of β-D-glucopyranose are dissolved in water, the initial specific optical rotation of +18.7° gradually increases to the equilibrium value of +53°. Mutarotation is both acid and base catalyzed.

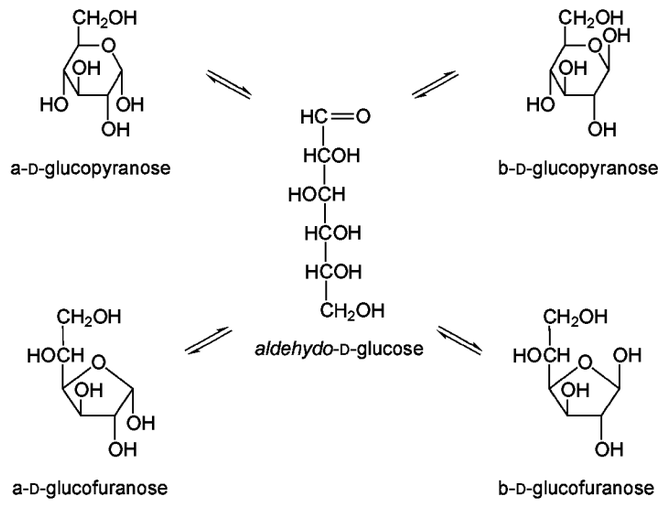
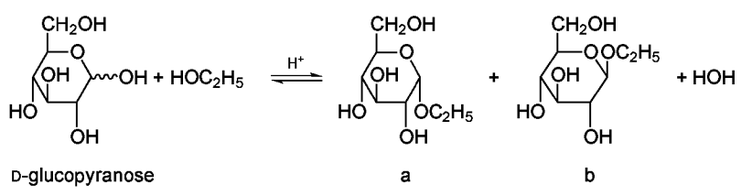


Fig. 3. Equilibrium mixture of D-glucose forms in solution. Pyranose ring forms predominate.

The structure of monosaccharides is often written in the acyclic form although only very minor amounts of it ever occur in that form. Because the interconversions are rapid, the carbonyl groups of sugars can and do react both as if they are free and as if they are in a hemiacetal ring form.

Glycosides, Oligosaccharides, and Polysaccharides. Few monosaccharides are found free in nature, and these few are usually present in only small amounts. Most monosaccharides occur in combinations, most often with either more of the same sugar or different sugars in the form of polymers (polysaccharides). Less frequently, except in the case of sucrose, they are joined together in oligosaccharide chains. Mono- and oligosaccharides may also be linked to nonsugar organic compounds. These combined forms of sugars are known as glycosides (1).

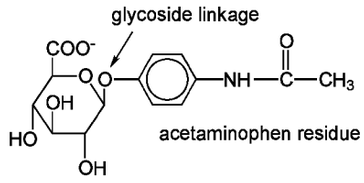
Pyranose and furanose ring forms of carbohydrate molecules are hemiacetals and can react with an alcohol to form glycosides, which are acetals of the sugars. Hydrolysis of a glycoside in an acidic solution releases the monosaccharide and the alcohol. This forward and reverse process is shown in the following for the reaction of D-glucose with ethanol to form ethyl α-D-glucopyranoside *[19467-01-7]* and ethyl β-D-glucopyranoside *[3198-49-0]*.



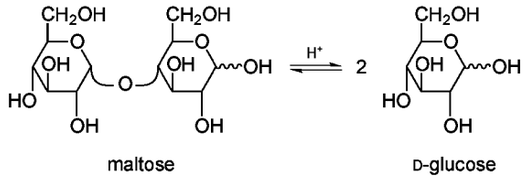
Glycosides, particularly of phenolic compounds, are widely distributed in plant tissues (2,10). Glycosides of anthocyanidins, flavones, flavanols, flavanones, flavanonols, stilbenes and saponins, gallic acid derivatives, and condensed tannins are all common.

In the body, detoxification of drugs and poisonous compounds often involves converting the substance into a more water-soluble compound which is then excreted in urine. The most common conversion reactions are hydroxylations, oxidations, reductions, and conjugations. Acetaminophen *[103-90-2]*, an analgesic used as an aspirin substitute, contains a hydroxyl group which is combined with the monosaccharide D-glucuronic acid to form the water-soluble β-D-pyranoside. After deacetylation, aspirin *[50-78-2]* may be conjugated with either D-glucuronic acid or the amino acid glycine. Uronic acids

are monosaccharides in which the terminal primary alcohol groups have been oxidized to a carboxylic acid functional group (11).



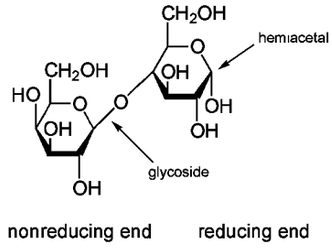
Frequently, the alcohol that forms a glycoside with a sugar is a hydroxyl group of another sugar. The formation of a glycoside between two sugar units joins them, forming a disaccharide, eg, two D-glucopyranosyl units may be linked to form the disaccharide maltose *[69-79-4]*.



Monosaccharide units are not joined together in such a simple acid catalyzed condensation, however. For chemical synthesis of di-and higher saccharides, activation of the anomeric carbon atom and blocking of hydroxyl groups not involved in the linkage are required and employed. An exception is found in the manufacture of polydextrose (Pfizer, Inc. and A. E. Staley Mfg. Co.) *[68424-04-4]*, which is made by heating under dehydrating conditions (vacuum) D-glucose, sorbitol (D-glucitol), and citric acid (catalyst) to make a highly branched, low molecular weight polymer.

For the most part, low molecular weight carbohydrates of commerce are made by depolymerization via enzyme- or acid catalyzed hydrolysis of polysaccharides. Only sucrose and, to a very much lesser extent, lactose, both disaccharides, are commercial low molecular weight carbohydrates not made in this way.

Oligo- and polysaccharides have reducing and nonreducing ends. A reducing sugar is a carbohydrate that contains an aldehyde or ketone group, either free or in a hemiacetal form, which in aqueous solution is always in equilibrium with the free form. The aldehyde group and the ketone group, after isomerization to an aldehyde group under basic conditions, can be oxidized to a carboxyl group, ie, act as a reducing agent. The reducing end of an oligo- or polysaccharide is the one end not involved in a glycosidic linkage and can, therefore, react as an aldehyde or ketone. The sugar units constituting all other ends are attached through glycosidic (acetal) bonds and are, therefore, nonreducing ends. Reducing and nonreducing ends can be demonstrated with the structure of lactose *[63-42-3]*, the reducing disaccharide of milk, β-D-galactopyranosyl-α-D-glucopyranose.



Additional sugar units added to either end of disaccharides form higher oligosaccharides. For example, if one α-D-glucopyranosyl unit is added to the disaccharide maltose, the trisaccharide maltotriose *[1109-28-0]* is obtained. Another unit extends to the tetrasaccharide maltotetraose *[34612-38-9]* and yet another to the pentasaccharide maltopentaose *[1668-09-3]*, and so on. Malto- is a prefix indicating a product originating from depolymerization of starch molecules. When many sugar units are joined together by glycosidic linkages, the structure is that of a polysaccharide.

Polysaccharides are naturally occurring polymers of monosaccharide (sugar) units (2,5–9). In precise chemical nomenclature, polysaccharides are glycans and are described as being composed of glycosyl units. Polysaccharides, like oligosaccharides, have ends that can be distinguished from each other because the individual monomer units are joined in a specific head-to-tail fashion. Polysaccharides have one reducing end (free or potential aldehyde or ketone group, although ketoses are uncommon constituents of polysaccharides) and at least one nonreducing end. Polysaccharide molecules can be linear or branched in any of several different ways (Fig. 4). They may be composed of a single type of glycosyl unit, a homoglycan, or from two to six different glycosyl units, a heteroglycan. They generally contain from hundreds to tens of thousands of glycosyl units; some may be larger. Of the heteroglycans, only the bacterial polysaccharides have regular repeating-unit structures because of a different pathway of biosynthesis as compared to plant and animal polysaccharides.

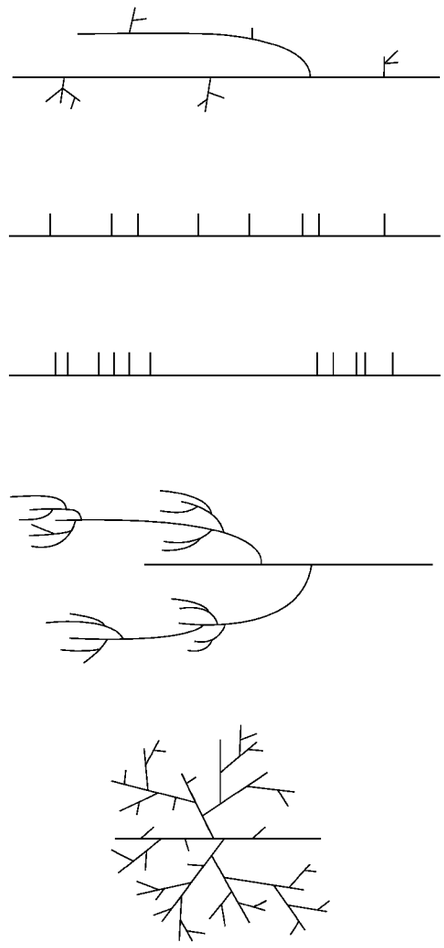


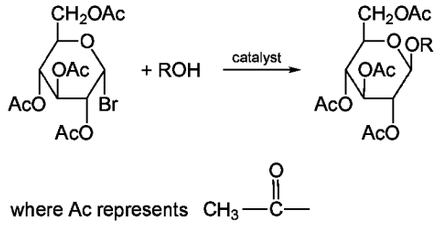
Fig. 4. Branching patterns in polysaccharides.

The polysaccharides of starch *[9005-25-8]* (12) are of great interest and importance. Because starch is the carbohydrate storage material of many plants and the principal component of corn, wheat, rice, potato, tapioca, arrowroot, sorghum, and other seeds and tubers, it is the principal source of carbohydrate in our diet. Starch is also widely used to make D-glucose, syrups, and related products. It is also a most important material in nonfood industries. Starch occurs in the form of granules composed of two polysaccharides. Both contain only α-D-glucopyranosyl units and are, therefore, glucans. One, amylose *[9005-82-7]*, is an essentially linear polysaccharide of (1 — 4)-linked α-D-glucopyranosyl units. Fine structure analysis has revealed that at least some, especially the larger molecules, are slightly branched. The basic structure of amylose, which is essentially an extension of the maltose structure shown previously, shows that there can be only one sugar unit in any polysaccharide that is not joined to another through a glycosidic bond involving its carbonyl group and only one reducing end. However, branching is possible in polysaccharides because of the multitude of OH groups. The second polysaccharide in starch granules, amylopectin *[9037-22-3]*, is a branched molecule.

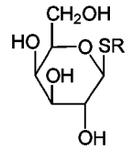
Glycogen *[9005-79-2]*, the principal carbohydrate food-reserve material in animals, has a structure similar to that of amylopectin, ie, it is a branched polymer consisting of linear segments of (1 — 4)-linked α-D-glucopyranosyl units joined by the (1 — 6) glycosidic linkages that constitute the branch points. All cells of higher animals may contain some glycogen. Because it is in a dynamic state, glycogen is polymolecular with the range of molecular weights depending on the metabolic state of the tissue. The weight-average molecular weight of rabbit liver glycogen was reported to be 2.7×10^8 daltons with a range of 6×10^6 to 1.6×10^9 daltons. It contains 0.35% of covalently-bound protein, a molecule that served as the primer upon which glycogenesis began. The average degree of polymerization (DP) of the chain segments depends on the source, but the majority of values are within the range DP 11–14. Glycogen is an amorphous polymer. It is highly soluble and exhibits a fairly ideal hydrodynamic behavior.

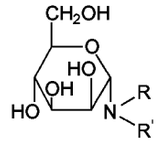
In commerce, hydrolysis of glycosidic bonds is far more important than is condensation of sugars with alcohols or other sugar units to form glycosidic bonds. Glycosidic bonds are formed in nature via biosynthetic reactions, and compounds containing them are isolated and used as starting materials for various transformations. Hydrolysis, whether catalyzed by acids or enzymes, follows the same general mechanism (1).

Synthetic Methods. Although mono- and oligosaccharides are most often made by depolymerization of polysaccharides, oligosaccharides and other compounds with glycosidic bonds can be made synthetically. The classic and still widely used reaction is the Koenigs-Knorr reaction; many modifications of it are known (1). The reaction in its simplest form is that given in equation 1. Modifications involve the nature of the catalyst and blocking groups and have been developed to influence the anomeric configuration, ie, the stereochemistry, of the product (13).



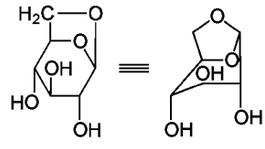
The activated sugar used in this reaction is 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide *[572-09-8]*, commonly called acetobromoglucose. A phenomenon known as the anomeric effect requires that this compound always have the α-D configuration, ie, that the halogen atom be in the axial position. Glycosyl chlorides and glycosyl fluorides are also used in the preparation of glycosides. The excocylic oxygen atom can also be replaced with a sulfur atom or an amino group (11).



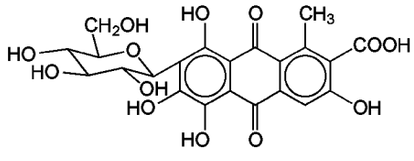


Nucleosides (2) and nucleotides are examples of the latter (glycosylamine) type.

The reaction to form an acetal can be an intramolecular reaction. The best known example is 1,6-anhydro-β-D-glucopyranose *[498-07-7]*, commonly called levoglucosan.



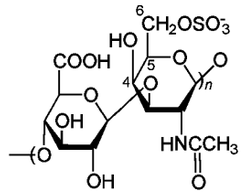
C-Glycosyl compounds have a carbon atom in place of the exocyclic oxygen atom of the acetal group and, therefore, are branched cyclic ethers. An example is the naturally occurring anthroquinone dye, carminic acid *[1260-17-9]* (CI Natural Red 4).



Glycoconjugates. Another class of carbohydrates are the glycoconjugates (14), composed of glycoproteins, proteoglycans, peptidoglycans, and glycolipids.

Glycoproteins (5,14–17) are molecules containing saccharide chains, often but not always oligosaccharide chains, covalently attached to a polypeptide chain. The saccharide chains may be attached via a glycosidic linkage to a hydroxyl group of a seryl, threonyl, hydroxylysyl, or hydroxyprolyl unit or via a glycosylamine linkage to the amide group of an asparaginyl unit. The percentage of carbohydrate in glycoproteins, which includes the majority of all proteins, varies from <1% to >80%. The surface of cells is covered with a complex mosaic of carbohydrates, called the glycocalyx, many of which are the saccharide units of glycoproteins. Some of those on erythrocytes control blood group antigenicity (see BLOOD, COAGULANTS AND ANTICOAGULANTS).

Proteoglycans (14,16,17) are components of connective tissue. They have specific polysaccharide chains covalently attached to a polypeptide chain. The specific polysaccharides are glycosaminoglycans (5,14,17,18), commonly called mucopolysaccharides. As the name suggests, these polysaccharides contain amino sugars (2-amino-2-deoxysugars). All except keratan sulfate contain uronic acid units; all except hyaluronic acid contain sulfate half-ester groups. The polysaccharides found as components of proteoglycans are chondroitin 4-sulfate *[24967-93-9]*, chondroitin 6-sulfate *[25322-46-7]*, dermatan sulfate *[24967-94-0]*, and keratan sulfate *[9056-36-4]*. The following structure is that of chondroitin 6-sulfate. In dermatan sulfate the –COOH group points down in the Haworth representation, ie, the uronic acid unit is an L-iduronic acid *[2073-35-0]* unit, and the sulfate group is at C-4.



There are other glycosaminoglycans. Hyaluronic acid *[9004-61-9]* occurs both free and in noncovalent association with proteoglycan molecules. Heparin *[9005-49-6]* and heparan sulfate *[39403-40-2]*, also known as heparitin sulfate *[9050-30-0]*, occur in mast cells and in the aorta, liver, and lungs.

Compounds with similar structures, ie, polysaccharide chains covalently attached to polypeptide chains, but where the polysaccharides are not glycosaminoglycans, are found commonly in plants and are known as protein-polysaccharides.

Peptidoglycans (14,16) are the primary component of bacterial cell walls. They consist of a heteropolysaccharide called murein cross-linked with short peptide chains.

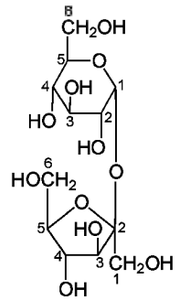
Glycolipids (5,14) are primarily glycosphingolipids, molecules that have oligosaccharide groups attached to ceramide *[104404-17-3]*. They are present, at least in small amounts, in the membranes of most, if not all, tissues. They too, like cell-membrane glycoproteins, are recognition determinants.

Lipopolysaccharides (14) are cell wall components of gram-negative bacteria.

Teichoic acids (16) are bacterial polymers in which alditols, glycerol, or ribitol are joined through the primary hydroxyl groups via phosphate diester linkages.

Phosphonomannans (7) are bacterial polymers in which manno-oligosaccharides are joined by phosphate diester linkages. Phosphonogalactans are present in certain fungi.

Sucrose and Derivatives of Sucrose. By far the most abundant of the naturally occurring oligosaccharides is the disaccharide sucrose *[57-50-1]*, ordinary table sugar from sugar cane or sugar beets (see SUGAR). The two monosaccharide units in sucrose are α-D-glucopyranosyl and β-D-fructofuranosyl units. In sucrose, the ketohexose, D-fructose *[30237-26-4]*, exists as a five-membered furanose ring (β-D-fructofuranose *[470-23-5]*) formed by reaction between the carbonyl group at C-2 and the hydroxyl group on C-5. This disaccharide is unique in that the two glycosyl units are linked head-to-head, ie, through an acetal bond rather than head-to-tail. Thus the molecule has no hemiacetal group and no reducing end, and is, therefore, classified as a nonreducing sugar.

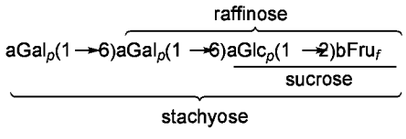


sucrose

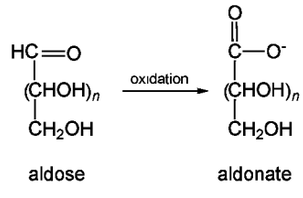
The trisaccharide raffinose *[512-69-6]*, which consists of a sucrose molecule with an α-D-galactopyranosyl unit linked 1 → 6 to its D-glucosyl unit, is the second most abundant oligosaccharide and, like sucrose, may be ubiquitous in the plant kingdom. However, it is present in only minor amounts as compared to sucrose.

The tetrasaccharide stachyose *[470-55-3]*, which contains an additional (1 → 6)-linked α-D-galactopyranosyl unit, is almost as widely distributed as raffinose, but is present in even lower concentrations. Although raffinose and stachyose occur in all parts of plants, they are concentrated in storage tissues, eg, sugar beets and beans, and leaves for the most part.

Structures of raffinose and stachyose are given below using official shorthand designations. In this system, the D or L designation is not used if the sugars are D; if a glycosyl unit is from an L sugar, an L is placed before the three-letter abbreviation. Subscripts *p* and *f* refer to pyranosyl and furanosyl rings, respectively.

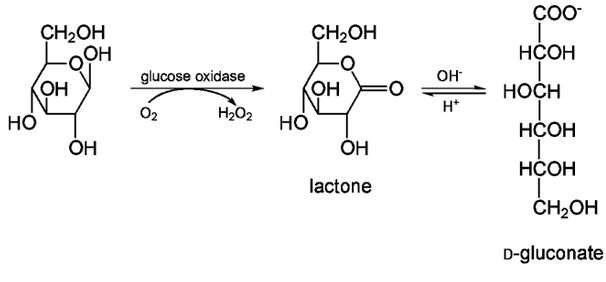


Oxidation to Sugar Acids and Lactones. When the aldehyde group of an aldose is oxidized, the resulting compound is an aldonic acid (salt form — aldonate) (11)4. Some aldonic acids are products of carbohydrate metabolism.

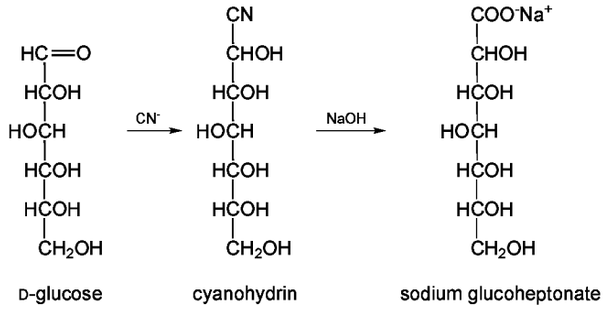


Oxidation of the aldehyde group of an aldose to form a carboxylic acid or carboxylic acid anion is often used analytically to determine the amount of reducing sugar. The Benedict and Fehling methods measure the amount of reducing sugar present in a fluid. In these reactions, the oxidant, Cu^{2+}, is reduced to Cu^{+}. Cu^{+} precipitates as Cu_2O, which can be measured in a variety of ways. In the Tollens test, Ag^{+} is reduced to Ag^{0}.

Monosaccharides in the pyranose or furanose ring forms can also be oxidized, forming an internal ester, a lactone, that can subsequently open to the acyclic form. The amount of D-glucose is often determined by this kind of oxidation catalyzed by an enzyme, glucose oxidase *[9001-37-0]*. Glucose oxidase-catalyzed oxidation of D-glucose is also used in the commercial production of D-glucono-1,5-lactone (D-glucono-δ-lactone) *[90-80-2]*, which is used for slow acidification, especially as a leavening agent (see BAKERY PROCESSES, CHEMICAL LEAVENING AGENTS).

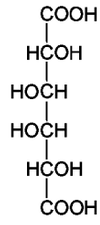


Preparation of another widely used aldonate, sodium glucoheptonate *[31138-65-5]*, involves reaction of D-glucose with cyanide ion. The cyanohydrin is then hydrolyzed to the heptonic acid salt. Both sodium D-gluconate *[527-07-1]* and sodium D-glucoheptonate are used as components of washing compounds because of their ability to sequester divalent cations, in agriculture to carry trace minerals, and in concrete (largest use). Both can be, and are, produced from glucose syrups as well as from pure crystalline D-glucose.



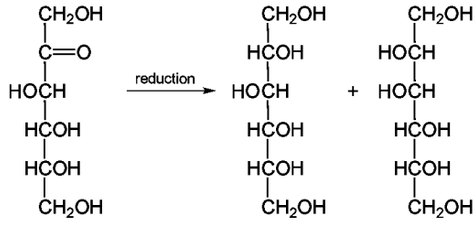
Oxidation of the carbon atoms at both ends of the carbon chain produces an aldaric acid. That made from D-galactose is galactaric acid *[526-99-8]*, a

meso compound commonly known as mucic acid.



galactaric acid

Reduction. Mono- and oligosaccharides can be reduced to polyols (polyhydroxy alcohols) termed alditols (glycitols) (1) (see SUGAR ALCOHOLS). Common examples of compounds in this class are D-glucitol (sorbitol) *[50-70-4]* made by reduction of D-glucose and xylitol *[87-99-0]* made from D-xylose. Glycerol *[56-87-5]* is also an alditol. Reduction of D-fructose produces a mixture of D-glucitol and D-mannitol *[69-65-8]*.



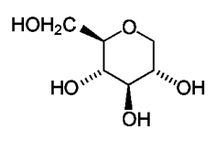
D-fructose D-glucitol D-mannitol

Sorbitol and mannitol are generally recognized as safe (GRAS). An important use of sorbitol is as a humectant. It can extend shelf life in confections and bakery products. Like other alditols, and unlike reducing sugars, it will not undergo Maillard browning and caramelization. Mannitol can be used as a dusting agent because of its low hygroscopicity. However, most food applications of alditols are in dietetic products.

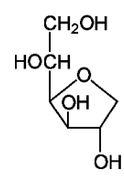
Alditols are sweet. Xylitol has essentially the same sweetness as sucrose; sorbitol is about half as sweet as sucrose. In chewing gum, polyols provide texture, sweetness, and mouthfeel and reduce the incidence of dental caries.

Reduction of oligomeric chains of monosaccharides results in the same oligosaccharide terminated at the reducing end with an alditol unit. Products made by hydrogenation of various corn syrups are viscous, hygroscopic, noncariogenic, and sweet, depending on the amounts of sorbitol and maltitol present. Their physical properties are generally similar to those of the syrup from which they are made, usually a high maltose syrup, but they exhibit a greatly decreased tendency to brown, a decreased tendency to crystallize, reduced fermentability, and slower conversion to D-glucose. The latter property makes these products of potential use as carbohydrate sources in diets for diabetics.

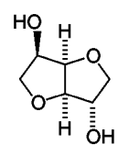
A series of sorbitol-based nonionic surfactants are used in foods as water-in-oil emulsifiers and defoamers. They are produced by reaction of fatty acids with sorbitol. During reaction, cyclic dehydration as well as esterification (primary hydroxyl group) occurs so that the hydrophilic portion is not only sorbitol but also its mono- and dianhydride. The product known as sorbitan monostearate *[1338-41-6]*, for example, is a mixture of partial stearic and palmitic acid esters (sorbitan monopalmitate *[26266-57-9]*) of sorbitol, 1,5-anhydro-D-glucitol *[154-58-8]*, 1,4-sorbitan *[27299-12-3]*, and isosorbide *[652-67-5]*. Sorbitan esters, such as the foregoing and also sorbitan monolaurate *[1338-39-2]* and sorbitan monooleate *[1338-43-8]*, can be further modified by reaction with ethylene oxide to produce ethoxylated sorbitan esters, also nonionic detergents FDA approved for food use.



1,5-anhydro-D-glucitol

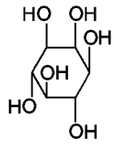


1,4-anhydro-D-glucitol
(1,4-sorbitan)



1,4:3,6-dianhydro-D-glucitol
(isosorbide)

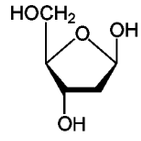
Cyclitols. Cyclitols are polyhydroxycycloalkanes and -alkenes (1,19). They are widely distributed in nature, though never in large quantities. The most abundant of these carbocyclic compounds are the hexahydroxycyclohexanes, commonly called inositols, and their methyl ethers. The nomenclature of cyclitols is problematic; several systems have been proposed and used. *myo*-Inositol *[87-89-8]* is so common in plants that it is generally regarded as being ubiquitous. It is most often found as ester, ether, and or glycoside derivatives. Phytic acid *[83-86-3]*, the hexakisphosphate monoester of myo-inositol occurs in most, if not all, higher plants. It is present in relatively large amounts in cereal grains and may be recovered as phytin, its mixed calcium–magnesium salt.



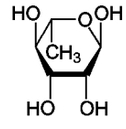
myo-inositol (a cyclitol)

REACTIONS OF HYDROXYL GROUPS

Reduction and Oxidation. Hydroxyl groups can be both oxidized to carbonyl groups (11) and removed by reduction. Sugars that have the hydroxyl group missing from one or more of the carbon atoms are called deoxy sugars. The sugar known by the common name 2-deoxy-D-ribose (2-deoxy-D-*erythro*-pentose) *[533-67-5]*, a component of DNA (deoxyribonucleic acid), is so designated because the hydroxyl group on C-2 of D-ribose is missing. A common component of polysaccharides is L-rhamnose (6-deoxy-L-mannose *[3615-41-6]*) as α-L-rhamnopyranosyl units.



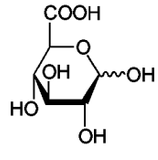
2-deoxy-b-D-ribofuranose



a-L-rhamnopyranose

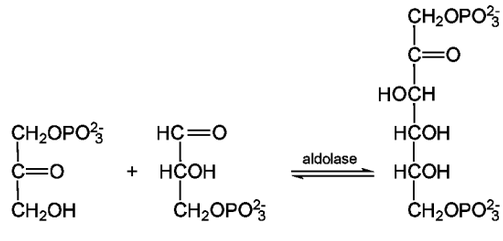
Oxidation of hydroxyl groups to carbonyl groups can form molecules with two aldehyde groups (dialdoses), two ketone groups (diuloses), or an aldehyde and a ketone group (osuloses). Keto acids are known as ulosonic acids.

Uronic acids are monosaccharides in which the terminal primary alcohol group is oxidized to a carboxylic acid functional group, eg, D-glucuronic acid *[6556-12-3]* (11).



D-glucuronic acid

Esterification. The hydroxyl groups of sugars can react with organic and inorganic acids just as other alcohols do. Both natural and synthetic carbohydrate esters are important in various applications (1,13). Phosphate monoesters of sugars are important in metabolic reactions. An example is the enzyme-catalyzed, reversible aldol addition between dihydroxyacetone phosphate *[57-04-5]* and D-glyceraldehyde 3-phosphate *[591-57-1]* to form D-fructose 1,6-bisphosphate *[488-69-7]*.



Naturally occurring ester groups also occur on polysaccharides, including phosphate, sulfate, acetate, glycolate, and succinate ester groups. Mono-, oligo-, and polysaccharides are often acylated to give them desirable functional properties. Examples are the fatty acid esters of sorbitol and 1,4-sorbitan already mentioned, fatty acid esters of sucrose used as biodegradable detergents, highly esterified cellulose acetate (acetate rayon), and starches with low degrees of phosphorylation (see CELLULOSE ESTERS).

Etherification. Carbohydrates are involved in ether formation, both intramolecularly and intermolecularly (1,13). The cyclic ether, 1,4-sorbitan, an 1,4-anhydroalditol, has already been mentioned. 3,6-Anhydro-α-D-galactopyranosyl units are principal monomer units of the carrageenans. Methyl, ethyl, carboxymethyl, hydroxyethyl, and hydroxypropyl ethers of cellulose (qv) are all commercial materials. The principal starch ethers are the hydroxyethyl and hydroxypropylethers (see CELLULOSE ETHERS; STARCH).

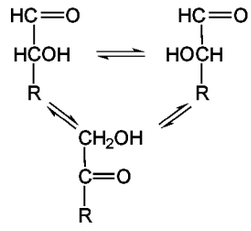
Acetalation. As polyhydroxy compounds, carbohydrates react with aldehydes and ketones to form cyclic acetals (1,13). Examples are the reaction of D-glucose with acetone and a protic or Lewis acid catalyst to form 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose *[582-52-5]* and its reaction with benzaldehyde to form 4,6-*O*-benzylidene-D-glucopyranose *[25152-90-3]*. The 4,6-*O*-(1-carboxyethylidine) group (related to pyruvic acid) occurs naturally in some polysaccharides.

Ester, ether, and cyclic acetal groups are used as blocking groups to allow regiospecific reactions to take place, ie, reaction at specific unblocked hydroxyl groups.

Replacement of Hydroxyl Groups. Replacement of a hydroxyl group with an amino group at any position produces an aminodeoxysugar (11,13,15). If the amino group is on the delta carbon atom from the carbonyl group, a six-membered ring containing –NH– will form. Thiosugars are ones in which a thiol group has replaced a hydroxyl group (11,13). When the thiol group is on the delta carbon atom from the carbonyl group, a six-membered ring containing –S– will form. Replacement of one or more hydroxyl groups with halogen atoms forms deoxyhalogenosugars (1).

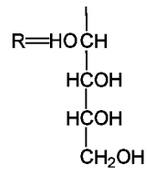
Isomerization. Both the carbonyl group and the adjacent hydroxyl group are involved in isomerization of monosaccharides. This reaction can be catalyzed by either a base or an enzyme. By this reaction, an aldose is converted into another aldose and a ketose, and a ketose is converted into two

aldoses. It is for this reason that ketoses are reducing sugars. They cannot act as reducing agents because they cannot be oxidized to acids, but especially under alkaline conditions, they can be isomerized to aldoses that are reducing agents.



isomerization

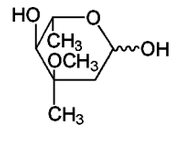
When this isomerization reaction is catalyzed by alkali, it is termed the Lobry de Bruyn-Alberda van Ekenstein reaction. By it, D-glucose, D-mannose, and D-fructose can be interconverted. The isomerizations involve a common intermediate, the 1,2-enediol. In the Glu–Man–Fru interconversions



Enzymes are specific, however. For example, starch is depolymerized using enzymes to D-glucose (dextrose). The solution of glucose is then treated with glucose isomerase *[9055-00-9]* to give D-fructose in about 42% yield. No D-mannose is formed. Addition of isolated D-fructose to this solution gives the common 55% high fructose corn syrup (HFCS) so widely used in soft drinks in the United States. HFCS is about 1.5 times as sweet as sucrose.

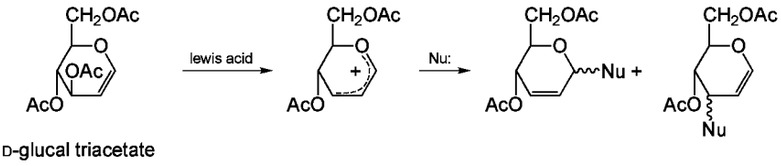
MODIFICATIONS OF THE CARBON CHAIN

Branched-chain sugars are found in nature, eg, cladinose, ie, 2,6-dideoxy-3-*C*-methyl-3-*O*-methyl-L-*ribo*hexose *[3758-45-0]*, a component of erythromycin.



cladinose

Unsaturated sugars are useful synthetic intermediates (11). The most commonly used are the so-called glycals (1,5- or 1,4-anhydroalditol-1-enes). In the presence of a Lewis-acid catalyst, 3,4,6-tri-*O*-acetyl-1,5-anhydro-2-deoxy-D-arabinohex-1-enitol *[2873-29-2]*, commonly called D-glucal triacetate, adds nucleophiles in both kinetically controlled and thermodynamically controlled (soft bases predominately at C-3 and hard bases primarily at C-1) reactions (11,13).

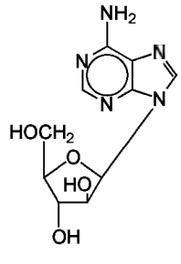


D-glucal triacetate

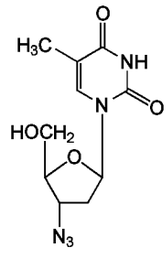
where Ac represents $CH_3-\overset{O}{\overset{\|}{C}}-$

Uses of Saccharides

Carbohydrates have widespread utilization, both as low cost, high volume commodities and as low volume specialty chemicals. Significant uses in terms of volume are surveyed here. Not covered are the lower volume uses involving carbohydrates either in the native state or in modified form; these are mainly pharmaceutical applications involving antibiotics, antigens, and synthetic drugs. In the latter case monosaccharides are becoming increasingly important as chiral synthons (chirons) as well as being used more directly to make products such as the nucleoside analogues AraA [9-(β-D-arabinofuranosyl)-9*H*-purin-6-amine] *[5536-17-4]*, an antineoplastic and antiviral compound known by a number of trade names, and AZT (3′-azido-3′-deoxythymidine *[30516-87-1]*), an antiviral compound also known by a variety of trade names (see ANTIVIRAL AGENTS).



AraA



AZT

The considerable uses of carbohydrates as carbon sources for various fermentations or the uses of unrefined carbohydrates, flours for example, are also not described here (see FERMENTATION).

MONOSACCHARIDES

D-Glucose is produced by complete depolymerization of starch with enzymes that catalyze the hydrolysis of both its (1 — 4) and (1 — 6) linkages. Crystalline α-D-glucopyranose is generally sold as dextrose. Glucose is also isomerized to D-fructose to produce high fructose corn syrup (HFCS). Crystalline D-fructose also finds use in the food industry. The annual consumption, in the United States, of dextrose is >600,000 tons and of HFCS >8,000,000 tons (71% solids basis).

OLIGOSACCHARIDES

Sucrose is widely used in the food industry to sweeten, control water activity, add body or bulk, provide crispness, give surface glaze or frost, form a glass, provide viscosity, and impart desirable texture. It is used in a wide variety of products from bread to medicinal syrups.

Lactose occurs in milk, mainly free, but to a small extent as a component of higher oligosaccharides. Cow and goat milks contain about 4.5% lactose; human milk contains about 7.0%. Lactose is used as an excipient in tablets to provide bulk and rapid disintegration. It is also used in some food products where it contributes body with only about 40% the sweetness of sucrose and enhances colors and flavors.

Oligo- and higher saccharides are produced extensively by acid-and or enzyme-catalyzed hydrolysis of starch, generally in the form of syrups of mixtures (12). These products are classified by their dextrose equivalency (DE), which is an indication of their molecular size and is a measure of their reducing power with the DE value of anhydrous D-glucose defined as 100.

Maltodextrins *[9050-36-6]* are mixtures of saccharides with average DE values of <20 (12). They are rather soluble, have a bland taste, and are widely used in foods. A dextrin is a product obtained by depolymerization of a polysaccharide.

Corn syrup solids are also dry products, have a smaller average size, and are comparatively sweeter (12). Both maltodextrins and corn syrup solids are used to prevent caking; enhance dispersibility and solubility; provide body or bulk; impart desirable texture; bind, carry, and protect flavors; control extrusion expansion; provide viscosity; form films and coatings; provide an oxygen barrier; inhibit crystallization; control sweetness; improve sheen; improve organoleptic characteristics; slow meltdown; and improve freeze–thaw stability.

Specifically prepared low DE starch products in the maltodextrin class, especially those from tapioca and potato starches, mimic a fatty mouthfeel and are used as fat replacers and or sparers (see FAT REPLACERS).

Another class of products are the cyclodextrins or cycloamyloses, a family of cyclic oligosaccharides containing α-D-glucopyranosyl units, most commonly seven (β-cyclodextrin *[7585-39-9]*, cycloheptaamylose, cyclomaltoheptaose) (20,21). All members of this class of compounds are made by action of a specific enzyme, cyclodextrin glycosyltransferase *[9030-09-5]*, on starch. In all, the glucosyl units are joined by (1 — 4) glycosidic linkages to form a ring, the cavity of which is especially useful for the formation of inclusion complexes with hydrophobic guest molecules. These stable complexes are potentially useful in the food industry to provide stable flavors and fragrances in dry powder form, in the pharmaceutical industry, and in other applications where increased chemical and or physical stability, solubility control, or controlled release is desired, for example, with agricultural chemicals (see INCLUSION COMPOUNDS).

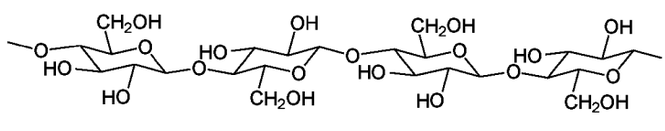
More extensive depolymerization of starch yields syrups. Syrups are purified, concentrated, aqueous solutions of saccharides with an average DE value of >20. Enzymes are most often used to make syrups, although combinations of acid- and enzyme-catalyzed hydrolyses and complete acid conversion may be used. Syrups are grouped into subclasses. Some contain as little as 35% of maltooligosaccharides. The maltooligosaccharides are both linear and branched, the branched structures arising from amylopectin. Products with progressively higher concentrations of lower molecular weight products are progressively sweeter and less viscous. By using proper conditions, syrups with specific defined compositions, for example, high maltose syrups, are prepared. The annual consumption in the United States of corn syrups is >3,000,000 tons (80.3% solids basis).

POLYSACCHARIDES

It has been estimated that >90% of the carbohydrate mass in nature is in the form of polysaccharides. In living organisms, carbohydrates play important roles. In terms of mass, the greatest amounts by far are structural components and food reserve materials, in that order and both in plants. However, carbohydrate molecules also serve as structural and energy storage substances in animals and serve a variety of other essential roles in both plants and animals.

Since polysaccharides are the most abundant of the carbohydrates, it is not surprising that they comprise the greatest part of industrial utilization (9,22). Most of the low molecular weight carbohydrates of commerce are produced by depolymerization of starch. Polysaccharide materials of commerce can be thought of as falling into three classes: cellulose, a water-insoluble material; starches, which are not water-soluble until cooked; and water-soluble gums.

Cellulose. Cellulose *[9004-34-6]* (qv) is the principal cell wall component of higher plants and the most abundant polysaccharide. Approximately one-half the mass of perennial plants and one-third the mass of annual plants is cellulose. It is a high molecular weight, linear, insoluble polymer of repeating β-D-gluco-pyranosyl units joined by (1 — 4) glycosidic linkages. Because of their linearity and stereoregular nature, cellulose molecules associate in extended regions, forming polycrystalline, fibrous bundles (23,24).



cellulose

High quality cellulose can be obtained from wood through pulping (delignification) and subsequent purification. The measure of the quality of cellulose is its content of alpha-cellulose, that portion insoluble in 18% alkali. Beta-cellulose is that portion which dissolves in 18% alkali, but precipitates when the solution is neutralized. Gamma-cellulose remains soluble after neutralization of the 18% alkali solution. The greatest amount of cellulose used is the purified, but not highly purified, wood pulp that is used in the manufacture of paper (qv), associated products, absorbants, rayons, and nonwovens. A

number of derivatives of cellulose are also commercial entities. The water-soluble ones are covered later.

Every polysaccharide contains glycosyl units with unsubstituted hydroxyl groups available for esterification or etherification. Polysaccharide derivatives are described by their degree of substitution (DS), which is the average number of substituent groups per glycosyl unit. Because each monomeric unit of cellulose molecules has free hydroxyl groups at C-2, C-3, and C-6, the maximum DS for cellulose, and all polysaccharides composed exclusively of neutral hexosyl units, the majority of polysaccharides, is 3.0.

Several cellulose esters (qv) are prepared commercially. Cellulose xanthate *[9032-37-5]* is made by reaction of cellulose swollen in 8.5–12% sodium hydroxide solution (alkali cellulose *[9081-58-7]*) with carbon disulfide and is soluble in the alkaline solution in which it is made. When such a solution, termed viscose, is introduced into an acid bath, the cellulose xanthate decomposes to regenerate cellulose as rayon fibers or cellophane sheets (see FIBERS, REGENERATED CELLULOSICS).

Cellulose acetate *[9004-35-7]*, prepared by reaction of cellulose with acetic anhydride, acetic acid, and sulfuric acid, is spun into acetate rayon fibers by dissolving it in acetone and spinning the solution into a column of warm air that evaporates the acetone. Cellulose acetate is also shaped into a variety of plastic products, and its solutions are used as coating dopes. Cellulose acetate butyrate *[9004-36-8]*, made from cellulose, acetic anhydride, and butyric anhydride in the presence of sulfuric acid, is a shock-resistant plastic.

Cellulose nitrate (pyroxylin) *[9004-70-0]*, made from cellulose and a mixture of nitric and sulfuric acids, is called gun cotton and is used in explosives. Nitrates of lower DS find some application in coatings and adhesives.

Ethylcellulose *[9004-57-3]*, a cellulose either (qv), as prepared commercially, ie, of high DS, is thermoplastic and has a low density (1.14 g cm^3). It forms films of good thermostability and excellent flexibility and toughness. Ethylcellulose is used in lacquers, inks, and adhesives and is combined with waxes and resins in the preparation of hot-melt plastics. It is also used as a pharmaceutical tablet binder.

Treatment of cellulose with acids results in preferential hydrolysis in the more accessible amorphous regions and produces a product known as microcrystalline cellulose (MCC). MCC is used to prepare fat-free or reduced-fat food products, to strengthen and stabilize food foams, as a tableting aid, and as a noncaloric bulking agent for dietetic foods. It has GRAS status.

Hemicelluloses and Related Polysaccharides. Hemicelluloses *[9034-32-6]* are a large group of polysaccharides that are associated with cellulose in the primary and secondary cell walls of all higher plants, but otherwise have no relationship to cellulose (2). They are also present in some other plants.

Hemicelluloses (qv) are heteroglycans. They do not comprise a distinct class of chemical structures. Constituent monosaccharides are D-xylose, D-mannose, D-glucose, D-galactose, L-galactose *[15572-79-9]*, L-arabinose, D-glucuronic acid, 4-*O*-methyl-D-glucuronic acid *[4120-73-4]*, D-galacturonic acid *[685-73-4]*, and to a lesser extent L-rhamnose, L-fucose, and various methyl ethers of neutral sugars, with a limit of perhaps six different glycosyl units per molecule. Both woody and nonwoody tissues contain 20–35% hemicelluloses. Some are neutral polymers, but most are acidic. The most abundant have a xylan backbone, ie, a chain of (1 → 4)-linked β-D-xylopyranosyl units. The chain my be linear, but is often branched and usually contains short side chains whether basically linear or branched. The most common acidic hemicelluloses are *O*-acetylated (4-*O*-methyl-D-glucurono)xylans *[9062-57-1]* and L-arabino-(4-*O*-methyl-D-glucurono)xylans *[69865-67-4, 9040-28-2, 98913-73-6]*, both often containing minor amounts of other sugar units as well. In the former, which are the preponderant hemicelluloses of woody angiosperms, the 4-*O*-methyl-α-D-glucopyranosyluronic acid units are most often joined to D-xylopyranosyl main chain units by (1 → 2) linkages. Some hemicelluloses have D-glucopyranosyluronic acid units as side chains, both the methylated and unmethylated forms in the same molecule being common. The number of uronic acid units varies considerably. Most hardwood xylans have approximately one uronic acid unit per 10 D-xylosyl units. The distribution is not uniform. Acetyl groups occur to the extent of 3–17%, with the greatest number being present in hardwood hemicelluloses.

The L-arabino-(4-*O*-methyl-D-glucurono)xylans are found in softwoods and annual plants. The L-arabinose is present primarily as α-L-arabinofuranosyl units, although β-L-arabinopyranosyl units may also be present. In either case, the arabinosyl units are often, but not always, present as single-unit side chains, as are the uronic acid units.

Cell walls of woods contain other subgroups of hemicelluloses, in particular those composed primarily of D-mannopyranosyl or D-galactopyranosyl units. Glucomannans *[11078-31-2]* comprise 3–5% of the wood of angiosperms and 3–12% of the wood of gymnosperms. Galactoglucomannans *[9040-29-3]* are also common.

Arabinogalactans *[9036-66-2]* appear to be ubiquitous in plant materials. They form a family of branched polysaccharides with backbones made up predominately of (1 → 3)-linked β-D-galactopyranosyl units with varying amounts of (1 → 6)-linked β-D-galactopyranosyl units. The L-arabinose is present primarily as L-arabinofuranosyl units. Some are attached to the backbone as single units; others may be in short chains. Nonreducing ends may be terminated with β-L-arabinopyranosyl units. Other units that may be present in arabinogalactans are L-rhamnopyranosyl (up to 11%), D-mannopyranosyl (up to 16%), D-xylopyranosyl (up to 7%), D-glucopyranosyl (up to 4%), D-glucopyranosyluronic acid and or 4-*O*-methyl-D-glucopyranosyluronic acid (up to 28%), and D-galactopyranosyluronic acid and or 4-*O*-methyl-D-galactopyranosyluronic acid (up to 26%) units. Not all arabinogalactans are acidic. Water-extractable arabinogalactans are abundant in the wood of larches. The fact that they are water-extractable indicates that they are not associated with lignin (qv) through chemical linkages or physical interactions and not involved in the construction of secondary cell walls. Therefore, larch arabinogalactans *[37320-79-9]* are probably not properly hemicelluloses.

Some hemicelluloses are partially extractable with water, but they are usually extracted with alkaline solutions following removal of lipids and lignin. Delignified plant material is termed, holocellulose. Neutralization of the alkaline extract effects precipitation of the more linear and less acidic hemicelluloses, termed the hemicellulose A *[63100-39-0]* fraction. The more acidic and more branched material, termed hemicellulose B *[63100-40-3]*, is precipitated with ethanol (70%). Hemicellulose B types type are usually water-soluble after extraction.

Certain cereal grains, especially wheat and rye, contain hemicelluloselike arabinoxylans *[9040-27-1]*, commonly called pentosans. Wheat flour pentosans are divided into two types: water-soluble and water-insoluble arabinoxylans, which respectively constitute ~1.1–1.6% and 0.4–0.7% of the total flour. These polysaccharides have functional roles in dough development and baking performance. The water-soluble wheat-flour arabinoxylans consist of a (1 → 4)-linked chain of β-D-xylopyranosyl units substituted at O-2 and or O-3 with single-unit α-L-arabinofuranosyl units. Preparations from each source consist of a family of molecules of various molecular weights and xyl:ara ratios.

Starches. Starch (qv) granules must be cooked before they will release their water-soluble molecules. It is common to speak of solutions of polysaccharides, but in general, they do not form true solutions because of their molecular sizes and intermolecular interactions; rather they form molecular dispersions. The general rheological properties of polysaccharides like the starch polysaccharides are described below under the discussion of polysaccharides as water-soluble gums. Starch use permeates the entire economy because it (corn starch in particular) is abundantly available and inexpensive. Another key factor to its widespread use is the fact that it occurs in the form of granules.

All green plants package and store carbohydrate (D-glucose) in the form of starch granules. In granule form, starch is quasi-crystalline (displays spherocrystalline patterns), dense, insoluble in cold water, and only partially hydrated. The sizes and shapes of granules are specific for the plant of origin. Granules can be easily isolated from suspensions by filtration or centrifugation, resuspended, reacted, and recovered (12,25).

Normal corn starch is composed of 20–30% of the linear polysaccharide amylose and 70–80% of the branched polysaccharide amylopectin. Amylose is a linear polysaccharide composed of (1 → 4)-linked α-D-glucopyranosyl units. Its degree of polymerization (DP), the number of monosaccharide units, is 200–22,000 (mol wt 32,000–3,600,000 daltons), depending on the source and method of preparation. Amylose can have several conformations. In the solid state it probably exists most often as a left-handed, sixfold helix. In solution, it seems to be a loosely wound and extended helix that behaves as a random coil. Amylopectin has a branch-on-branch structure. Amylopectin molecules are composed of chains of α-D-glucopyranosyl units joined by (1 → 4) linkages; branches are formed by joining these chains with α-D-(1 → 6) linkages. The average chain length (CL) is 20–30, although branch points are not equally spaced. In the currently accepted model of an amylopectin molecule, the branches occur in clusters. The molecular weight of amylopectin has been measured as 5×10^7 2×10^8 daltons (DP3 $\times 10^6$ 2.5×10^6), depending on the source and method of preparation. Granules of waxy types of maize, sorghum, rice, and barley contain only amylopectin molecules. Potato starch amylopectin occurs as a natural phosphate ester (12).

Through genetic manipulation, corn cultivars with altered starch compositions have been developed. Various modified and derivatized starches are

produced by treating a slurry of starch granules with chemicals or enzymes (12,22,25). After treatment, the products are again recovered, washed, and dried. Although these modifications and derivatizations are done to effect significant improvements in physical properties, the amount of chemical change may only need to be very slight to effect functional property alteration.

Oxidized Starches. Alkaline hypochlorite treatment introduces carboxyl and carbonyl groups, effects some depolymerization, and produces whiter (bleached) products that produce softer, clearer gels. Ammonium persulfate is used in some paper mills with continuous thermal cookers to prepare *in situ* high solids, low viscosity dispersions. Most of the hypochlorite-oxidized starch and all the ammonium persulfate-oxidized starch is used in the paper industry. The low solution viscosity and good binding and adhesive properties of these products make them especially effective in high solids, pigmented coatings.

Dextrins. Dextrins *[9004-53-9]*, like oxidized starches, are in the class of so-called converted starches. Dextrins are produced by dry heating starch with or without a catalyst (acidic or alkaline). Because there are a number of variables in the process, a wide range of dextrins with widely varying properties can be produced. All are characterized by higher solubility, lower viscosity, film-forming ability, and loss of the ability to gel. High solids solutions of some of the more highly converted dextrins produce the tacky, quick-setting adhesives used in paper products.

Acid-Modified Starches. Acid-modified starches are prepared by treating a suspension of starch granules with dilute mineral acid. In this process, a small amount of glycosidic bond hydrolysis occurs, resulting in products that produce much less viscosity. A concurrent weakening of the granule structure occurs. The result is that there is more granule disintegration, but less granule swelling, when acid-modified starches are heated in water; and although they have reduced viscosity-imparting power, they form gels with improved clarity and increased strength. These acid-modified starches, also called thin-boiling and acid-thinned starches, are used in large quantities as textile warp sizes.

Starch Ethers. A large number of starch ethers have been prepared and patented; only a few are manufactured and used commercially. Commercially available starch ethers are the hydroxyalkyl ethers, hydroxyethylstarch *[9005-27-0]* and hydroxypropylstarch *[9049-76-7]*, and cationic starches.

Essentially all starch derivatives are made by adding the required reagent (in this case, ethylene oxide or propylene oxide) to an agitated, slightly alkaline (pH 7–12), aqueous starch suspension (35–45% solids) at a slightly elevated temperature. After the required reaction time, the derivatized granules are recovered, washed, and dried. The majority of starch derivatives have degrees of substitution of <0.1. Monofunctional starch derivatives are made to increase starch paste stability. Increased stability results from the introduction of substituent groups that interfere with intermolecular associations.

Hydroxyethylstarch is widely used with synthetic latexes in the surface sizing of paper and as a coating binder. For these uses, the hydroxyethylstarch is acid-thinned, oxidized, or dextrinized. Hydroxypropylstarch is used in foods to provide viscosity stability and to ensure water-holding during low temperature storage.

Starch Esters. As with the starch ethers, a large number of starch esters have been prepared and patented, but only a few are manufactured and used commercially. Both inorganic and organic acid esters can, and have been, made. The latter are prepared by the same general procedure used to make starch ethers.

Starch acetates *[9045-28-7]* are made by reaction of starch with acetic anhydride. Starch acetates are used in foods to provide paste clarity and viscosity stability at low temperatures. A waxy maize starch acetate is most commonly used. Waxy maize starch acetates for food use are often cross-linked. Acetylated starches are also widely used in warp sizing of textiles.

Starch succinates *[39316-70-6]* are also used as thickening agents in foods. The 1-octenylsuccinate half-ester *[52906-93-1]*, sold as its sodium salt *[66829-29-6]*, has surface active (emulsifying) properties.

Starch sodium phosphate monoesters *[11120-02-8]* are prepared by heating mixtures of 10% moisture starch and sodium monohydrogen and dihydrogen phosphates or sodium tripolyphosphate. Starch phosphate monoesters are used primarily in foods, such as pudding starches and with oil-in-water emulsions.

Cross-linked Starches. The polymer chains in starch granules can be cross-linked with difunctional reagents that form diethers or diesters. The properties imparted to the starch by such cross-linking are unique and, therefore, these derivatives are considered separately. Diphosphate ester cross-links can be introduced by reaction of starch with phosphoryl chloride or sodium trimetaphosphate. Glycerol diethers of starch are made by reaction of starch with epichlorohydrin, although this reaction is no longer used in the United States to prepare modified food starch. A small amount of cross-linking, eg, 1 cross-link per 1000–1300 D-glucopyranosyl units, greatly reduces both the rate and the degree of granule swelling and the sensitivity of starch slurries to processing conditions such as temperature, shear, and acids.

Cross-linking is employed when a stable, high viscosity starch paste is needed and particularly when the dispersion is to be subjected to high temperature, high shear, and or low pH. Food starches, especially those made from waxy maize, potato, and tapioca starch are usually both cross-linked and phosphorylated, acetylated, or hydroxypropylated to provide appropriate gelatinization, viscosity, and textural properties. Examples of their application are their use in canned foods that are to be retort-sterilized and in the preparation of spoonable salad dressings where products stable to high shear at low pH are required. Higher degrees of cross-linking give starches that do not gelatinize, even under autoclave conditions.

Cationic Starches. Commercial cationic starches are starch ethers that contain a tertiary amino or quaternary ammonium group, eg, the diethylaminoethyl ether of starch or the 2-hydroxy-3-(trimethylammonio)propyl ether of starch *[9063-45-0]*, sold as its chloride salt *[56780-58-6]*.

Cationic starches are used in papermaking. When they are used as a wet-end additive, affinity between the cationic starch and cellulose fibers, which have a negative charge, results in almost complete and irreversible adsorption of the starch. Cationic starches are also used in surface sizing of paper and as coating binders. Amphoteric starches made by introducing anionic groups, such as phosphate monoester or sulfosuccinate ester groups or carboxyl groups produced by oxidation, to cationic starches give improved performance in some applications.

Pregelatinized Starches. Suspensions of starches and starch derivatives can be gelatinized cooked and dried to yield a variety of products that can be dispersed in cold water to yield pastes comparable to those obtained by cooking granular starch products. These products are made for convenience of use.

Starch Graft Copolymers. A product made by polymerizing acrylonitrile *[107-13-4]* onto gelatinized starch, converting the resulting nitrile groups into a mixture of carbamoyl and alkali metal carboxylate groups by treatment with alkali, and drying will reversibly absorb many hundreds of times its weight of water without dissolving. This product finds use as an additive to absorbent soft goods, such as disposable diapers, incontinent pads, hospital bed pads, bandages and catamenials, in base root coating of nursery stock, in seed coating, and in hydrogel wound dressing.

Cold-Water Swelling Starches. Special physical treatment produces starch granules that will swell in water without heating. Molecular dispersions can be formed by application of shear to the swollen granules.

General Properties of Starches. Heating a starch in water causes the granules to swell. At sufficient solids concentration the swollen granules occupy most of the space and a viscous mass, called a paste, results. Application of shear to these fragile, swollen granules results in formation of a molecular dispersion. The process of granule swelling with concurrent hydration and solubilization of starch molecules is called gelatinization. Gelatinization is accompanied by a loss of birefringence. The temperature at which this occurs is called the gelatinization temperature.

The viscosity obtained by cooking a suspension of starch is determined by the starch type, derivatization and or modification, solids concentration, pH, amount of agitation during heating, rate of heating, maximum temperature reached, time held at that temperature, agitation during holding, and the presence of other ingredients.

An aqueous dispersion of an unmodified starch containing amylose will gradually form an insoluble precipitate through association of linear segments. This process is called retrogradation or set-back.

The properties of amylose and amylopectin are reflected in the starches. For example, high amylose starches are difficult to gelatinize because of the extra energy needed to disassociate and hydrate the aggregates of amylose; form firm, opaque gels; and can be used to make strong, tough films. Its solutions and gels will undergo retrogradation. Waxy maize starches, even when they are underivatized, gelatinize more easily and yield viscous, almost transparent solutions that will not form firm gels.

In general, derivatization increases solution and gel clarity, reduces the tendency to gel, improves water binding, increases freeze–thaw stability, reduces the gelatinization temperature, increases peak viscosity, and reduces the tendency to retrograde. Combinations of substitutions are used to obtain desired properties for specific applications.

Water-Soluble Gums. Gums (qv) are polymeric substances which, in an appropriate solvent or swelling agent, form highly viscous dispersions or gels at low dry substance content. Commonly, the term industrial gums refers to water-soluble polysaccharides, glycans in official carbohydrate nomenclature, or polysaccharide derivatives used industrially. They are classified both by structure (Table 1) and by source (Table 2). Particularly in the food industry, the term hydrocolloid is often used interchangeably with gum.

Table 1. Classification of Selected, Native Polysaccharides by Structure

	Examples
Classification by shape[a]	
linear	algins, amyloses, carrageenans, cellulose, chondroitins, chitins, colominic acid [poly(*N*-acetyl-neuraminic acid], curdlan, dermatan sulfate, furcellaran, gellan, glucomannans, heparin, hyaluronic acid, inulin, keratan sulfate, laminarans[b], mannans, nigeran, pectic acids, pectins, pullulan
branched	
short branches on an essentially linear backbone	arabinans[c], arabinogalactans, galactoglucomannans, galactomannans, konjac mannan, protopectins, psyllium seed gum, rhamsan, scleroglucan, succinoglycan, welan, xanthan, xylans, xyloglucans
branch-on-branch structures	amylopectins, arabinoxylans, flaxseed polysaccharide (acidic), glycogens, gum arabics, gum ghatti, gum karaya, gum tragacanth (tragacanthin), okra gum
Classification by monomeric units[d]	
homoglycans	amylopectins, amyloses, arabinans, cellulose, chitins, colominic acid, curdlan, glycogens, laminarans,[b] mannans, nigeran, pullulan, scleroglucan
diheteroglycans	algins, arabinogalactans, carrageenans, chondroitins, furcellarans, galactomannans, glucomannans, hyaluronic acid, inulin, keratan sulfate, konjac mannan, pectic acids, pectins, succinoglucan, xylans
triheteroglucans	arabinoxylans, dermatan sulfates, galactoglucomannans, gellan, gum karaya, heparin, rhamsan, xanthan
tetraheteroglycans	flaxseed polysaccharide (acidic), gum arabics, okra gum, psyllium seed gum, welan, xyloglucans
pentaheteroglucans	gum ghatti, gum tragacanth (tragacanthin), protopectins
Classification by charge	
neutral	amylopectins, amyloses, arabinans, arabinogalactans, cellulose, chitins, curdlan, galactoglucomannans, galactomannans, glucomannans, glycogens, inulin, laminarans, mannans, konjac mannan, nigeran, pullulan, scleroglucan, xyloglucans
anionic (acidic)[e]	algins, arabinoxylans, carrageenans, chondroitins, colominic acid, dermatan sulfates, flaxseed polysaccharide, furcellarans, gellan, gum arabics, gum ghatti, gum karaya, gum tragacanth (tragacanthin), heparin, hyaluronic acid, keratan sulfate, okra gum, pectic acids, pectins, protopectins, psyllium seed gum, rhamsan, succinoglycan, welan, xanthan, xylans
cationic	chitosans (not native)

[a] Primary examples. For example, arabinoxylans occur in different architectures, compositions, and charges.

[b] Contains a few long-chain branches. Some chains are terminated at the reducing end with a second type of unit.

[c] The predominate structure.

[d] Considers only the basic monosaccharide units. A derivatized monosaccharide unit, such as a D-galactopyranosyl 6-sulfate unit, is not considered as a unit separate from a D-galactopyranosyl unit, for example.

[e] From the presence of uronic acid, sulfate half-ester, pyruvyl cyclic acetal, or succinate half-ester groups.

Table 2. Classification of Commercial Polysaccharides by Source

Class	Examples
algal (seaweed) extracts	agars, algins, carrageenans, furcellarans, laminarans
higher plants	
insoluble	cellulose
extract	pectins
seeds	corn starches, wheat starch, guar gum, locust bean gum, psyllium seed gum
tubers and roots	potato starch, tapioca starch, konjac mannan
exudates	gum arabics, gum karaya, gum tragacanth
microorganisms (fermentation gums)	curdlan, dextrans, gellan, pullulan, scleroglucan, welan, xanthans
animal	chitins chitosans
derived	
from cellulose	carboxymethylcelluloses, cellulose acetates, cellulose acetate butyrates, cellulose nitrates, ethylcellulose, hydroxyalkylcelluloses, hydroxyalkylalkylcelluloses, methylcelluloses
from starch	starch acetates, starch 1-octenylsuccinates, starch phosphates, starch succinates, hydroxyethylstarches, hydroxypropylstarches, cationic starches, oxidized starches, dextrins
from guar gum	carboxymethylguar gum, carboxymethyl(hydroxypropryl)guar gum, hydroxyethylguar gum, hydroxypropylguar gum, cationic guar gum
synthetic	polydextrose

The usefulness of such industrial gums is based on their physical properties, in particular their capacity to thicken and or gel aqueous solutions and otherwise to control water. Because all gums modify or control the flow of aqueous solutions, dispersions, and suspensions, the choice of which gum to use for a particular application often depends on its secondary characteristics. These secondary characteristics are responsible for their utilization as adhesives, binders, bodying agents, bulking agents, crystallization inhibitors, clarifying agents, cloud agents, emulsifying agents, emulsification stabilizers, encapsulating agents, film formers, flocculating agents, foam stabilizers, gelling materials, mold release agents, protective colloids, suspending agents, suspension stabilizers, swelling agents, syneresis inhibitors, texturing agents, and whipping agents, in coatings, and for water absorption and binding.

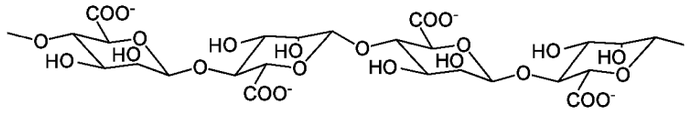
Gums are tasteless, odorless, colorless, and nontoxic. None, except the starches and starch derivatives, are broken down by human digestive enzymes. All are subject to microbiological attack. All can be depolymerized by acid- and enzyme-catalyzed hydrolysis of the glycosidic (acetal) linkages joining the monomeric (saccharide) units.

All native and modified polysaccharides have a range of molecular weights, and the average composition and distribution of molecular weights in a gum sample can vary with the source, the conditions used for isolation or preparation, and any subsequent treatment(s). In all except bacterial polysaccharides, the percentage of individual monomeric unit types varies from molecule to molecule and from sample to sample. Because both molecular size and structure determine physical properties, various functional types of a given gum are produced by controlling the source and isolation procedure (in the case of natural gums) or derivatization method (in the case of derived gums) and subsequent treatment(s).

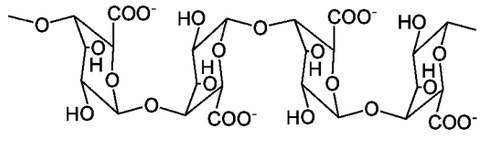
In general, gums do not form true solutions because of their molecular weights and intermolecular interactions. Rather they form molecular dispersions. The rheology or flow characteristics and gel properties of gum solutions is a function of particle size, particle shape, particle flexibility and ease of deformation, particle solvation, and the presence and magnitude of charges, where the particles may be dispersed molecules and or aggregated clusters of molecules. In general, the rheology of gum solutions is pseudoplastic or thixotropic, ie, they exhibit shear thinning. Most gums are available in a range of viscosity grades.

Polysaccharide gels generally are composed of 99.0–99.5% water and 0.5–1.0% gum. Important characteristics of gels are means of gelation (chemical gelation, thermogelation), reversibility, texture (brittle, elastic, plastic), rigidity (rigid or firm, soft or mushy), tendency for syneresis, and cutable or spreadable. Gels are composed of interconnected fringed micelles.

Algins. Algins are salts (generally sodium *[9005-38-3]*, ammonium *[9005-34-9]*, or potassium *[9005-36-1]*) or esters (propylene glycol) of alginic acid. Alginic acid *[9005-32-7]* is a generic term for polymers of D-mannuronic acid and L-guluronic acid. Alginic acid molecules contain at least three different types of polymer segments: poly(β-D-mannopyranosyluronic acid) segments, poly(α-L-gulopyranosyluronic acid) segments, and segments with alternating sugar units. The ratios of the constituent monomers and the chain segments vary with the source and determine the specific properties of the preparation. All linkages are 1 — 4, making alginates linear polymers. The shapes of the poly(D-mannopyranosyluronic acid) and the poly(L-gulopyranosyluronic acid) segments are quite different because the β-D-mannopyranosyluronic acid units are in the $^4C_1$ conformation and diequatorially linked, whereas the α-L-gulopyranosyluronic acid units are in the $^1C_4$ conformation and diaxially linked. The different conformations make the former segments flat and the latter buckled.



a poly(b-D-mannuronosyl) segment



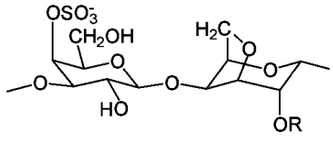
a poly(a-L-guluronosyl) segment

Algins are extracted from brown algae (*Phaeophyceae*). The primary U.S. source is the beds of giant kelp (*Macrocystis pyrifera*) that grow off the coast of southern California. The polymer is extracted by treating the seaweed with a sodium carbonate solution. It is recovered from the extract by precipitation as alginic acid or as the calcium salt *[9005-35-0]*, which is then washed with acid to convert it into alginic acid. The alginic acid is then treated with a base to convert it into the desired salt or partially neutralized alginic acid is treated with propylene oxide to make the propylene glycol ester *[9005-37-2]*.

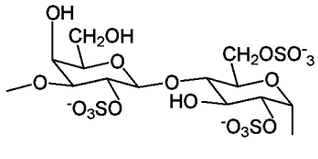
An important and useful property of alginates is their ability to form gels by reaction with calcium ions. Different types of gels are formed with alginates from different sources. Alginates with a higher percentage of polyguluronate segments form the more rigid, more brittle gels which tend to undergo syneresis. Alginates with the higher percentage of polymannuronate segments form the more elastic, more deformable gels, which have a reduced tendency to undergo syneresis.

Carrageenans, Agars, and Furcellarans. Carrageenan is a generic term applied to polysaccharides extracted from a number of closely related species of red seaweeds. Agar *[9002-18-0]* and furcellaran *[9000-21-9]* are also red seaweed extracts and are members of the same larger family. All polysaccharides in this family are derivatives of linear galactans. All have alternating monosaccharide units and linkages. In all members of the family, one sugar unit is a β-D-galactopyranosyl unit with a glycosidic linkage to O-3. In all except agar, the other unit is a 3,6-anhydro-α-D-galactopyranosyl unit with a glycosidic linkage to O-4. In agar, the other unit is a 3,6-anhydro-α-L-galactopyranosyl unit.

Commercial carrageenans are composed primarily of three types of polymers: kappa-, iota-, and lambda-carrageenan.



kappa-carrageenan, R = H
iota-carrageenan, R = SO^-_3



lambda-carrageenan

Their molecular weights average about 250,000 daltons. The half-ester sulfate contents are 0–3% in agarose *[9012-36-6]*, more properly termed agaran, the linear component of agar, 12–16% in furcellaran, ca 25% in kappa-carrageenan *[1114-20-8]*, ca 32% in iota-carrageenan *[9062-07-1]*, and ca 35% in lambda-carrageenan *[9064-57-1]*. Each polymer is heterogeneous. Each commercial gum is believed to be generated during production from native precursor polysaccharides.

Kappa- and iota-carrageenans exist as right-handed, threefold helices that form double helices reversibly. The double-helical segments of kappa- and

iota-carrageenans can then interact to form a three-dimensional gel network. The conformation of lambda-carrageenan, a nongelling gum, has been described as a zigzagging ribbon.

Carrageenans and agars are structural polysaccharides of the *Rhodophyceae*, the red algae. Carrageenans are extracted primarily from *Chondrus* and *Gigartina* species. Furcellaran is obtained primarily from *Furcellaria* species. Agars are obtained primarily from *Gelidium* and *Gracilaria* species.

A useful property of the red seaweed extracts is their ability to form gels with water and milk. Kappa-carrageenan reacts with milk protein micelles, particularly kappa-casein micelles. The thickening effect of kappa-carrageenan in milk is 5–10 times greater than it is in water; at a concentration of 0.025% in milk, a weak thixotropic gel is formed.

Agars are the least soluble of this class of polysaccharides; they can be dispersed only at temperatures above 100°C. When agar dispersions are cooled, strong, brittle, turbid gels form. Agar gels remelt when heated, synerese, and are unstable to freeze–thaw cycles. By far the greatest use of agar in the United States is in the preparation of microbiological culture media. Agar is also used in dental impression materials and in bakery icings. Agar and agarose are used in making gels for electrophoresis, in gel-filtration chromatography, and in several applications in biotechnology.

Guar and Locust Bean Gums. Guaran, the purified polysaccharide from guar gum *[9000-30-0]*, is a galactomannan *[11078-30-1]*. It has a mannan backbone, a linear chain of (1 → 4)-linked β-D-mannopyranosyl units with, on the average, one of every 1.8 mannosyl units substituted with a (1 → 6)-linked α-D-galactopyranosyl unit. The mannan chain is rather evenly substituted with D-galactopyranosyl units but still contains some unsubstituted or smooth regions. Its molecular weight is 220,000 ± 20,000 daltons (DP 1360 ± 125).

Like guaran, and the endosperm polysaccharides of other legumes, locust bean (carob)gum *[9000-40-2]* is also a galactomannan. Like guaran, it has a linear backbone of (1 → 4)-linked β-D-mannopyranosyl units. However, in locust bean gum, approximately one of every 3.9 β-D-mannopyranosyl units, on the average, is substituted with an α-D-galactopyranosyl unit attached at O-6.

Commercial guar gum is not purified guaran but the ground endosperm of guar seeds. Guar gum forms very high viscosity, pseudoplastic solutions at low concentrations. Guar endosperm preparations can be derivatized with the same reagents and catalysts used to modify starch and cellulose. The following products are prepared by proprietary processes: hydroxypropyl- *[39421-75-5]*, hydroxyethyl- *[39465-11-7]*, sodium carboxymethyl- *[51190-15-3]*, sodium carboxymethyl(hydroxypropyl)- *[39454-79-0]*, and 2-hydroxy-3-(trimethylammonio)propyl- *[67034-33-7]*, (made as its chloride salt *[65497-29-2]*) guar gums. Derivatives are made to control the rate of hydration, peak viscosity, ash content, insoluble material, heat stability, and compatibility with other materials.

Polymer chains of guar gum and its derivatives, in fact of all galactomannans, are readily cross-linked with borate and titanium ions. Gels formed in this way are rubbery in nature.

Commercial locust bean gum is the ground endosperm of the seeds of the locust bean (carob) tree. The general properties of locust bean gum are similar to those of guar gum. Differences are its low cold-water solubility and its synergistic gelation with kappa-carrageenan, furcellaran, and xanthan *[11138-66-2]*.

Gum Arabic. Of the gums of ancient commerce, which were dried, gummy exudations collected by hand from various trees and shrubs, only gum arabic *[9000-01-5]*, also called gum acacia and acacia gum, is still in significant use. Gum arabic preparations are mixtures of highly branched, branch-on-branch, acidic polysaccharides. The polysaccharides have a branched main chain of β-D-galactopyranosyl units. Attached to this backbone are side chains containing L-arabinofuranosyl, L-rhamnopyranosyl, D-galactopyranosyl, and D-glucopyranosyluronic acid units in varying amounts depending on the source. Generally accepted values for number average and weight average molecular weights are 250,000 and 580,000 daltons, respectively; these values correspond to DPs of 155 and 3600.

Gum arabic comes from various species of *Acacia*. The gum exudes through cracks, injuries, and incisions in the bark and is collected by hand as dried tears. Gum arabic is unique among gums because of its high solubility and the low viscosity and Newtonian flow of its solutions. While other gums form highly viscous solutions at 1–2% concentration, 20% solutions of gum arabic resemble a thin sugar syrup in body and flow properties.

Pectins. While there is no agreed upon definition of pectic substances, general usage is as follows. Pectic acids *[9046-40-6]* are galacturonoglycans [poly(α-D-galactopyranosyluronic acids)] *[9046-38-2, 84149-03-1, 25249-06-3]* without, or with only a negligible content of, methyl ester groups. Pectic acids have various degrees of neutralization. Salts of pectic acids are pectates. Pectinic acids are galacturonoglycans with various, but greater than negligible, contents of methyl ester groups. Pectinic acids may have varying degrees of neutralization. Salts of pectinic acids are pectinates. Pectins *[9000-69-5, 16048-08-1, 58128-44-2]* are mixtures of polysaccharides that originate from plants, contain pectinic acids as primary components, are water-soluble, and whose solutions will gel under suitable conditions. The term pectin is often used in a generic sense to designate those water-soluble galacturonoglycans of varying methyl ester content and degree of neutralization that are capable of forming gels. Commercial pectins have been altered by the conditions of extraction. In the native state, pectin is known by protopectin *[9012-27-5]*, a more complex molecule.

Pectins are subdivided according to their degree of esterification (DE), a designation of the percent of carboxyl groups esterified with methanol. Pectins with DE >50% are high methoxyl pectins (HM pectins) *[65546-99-8]*; those with DE <50% are low methoxyl pectins (LM pectins) *[9049-34-7]*. The degree of amidation (DA) indicates the percent of carboxyl groups in the amide form.

The key feature of all pectin molecules is a linear chain of (1 → 4)-linked α-D-galactopyranosyluronic acid units, making it an α-D-galacturonan [a poly(α-D-galactopyranosyluronic acid) or an α-D-galacturonoglycan] *[9046-38-2, 84149-03-1, 25249-06-3]*. In all natural pectins, some of the carboxyl groups are in the methyl ester form. Depending on the isolation conditions, the remaining free carboxylic acid groups may be partly or fully neutralized. The DE strongly influences the solubility, gel-forming ability, conditions required for gelation, gelling temperature, and gel properties of the preparation.

Inserted L-rhamnopyranosyl units may provide the necessary irregularities (kinks) in the structure required to limit the size of the junction zones and produce a gel. The presence of side chains composed of D-xylosyl units may also be a factor that limits the extent of chain association. Junction zones are formed between regular, unbranched pectin chains when the negative charges on the carboxylate groups are removed (addition of acid), hydration of the molecules is reduced (addition of a cosolute to a solution of HM pectin), and or pectinic acid polymer chains are bridged by multivalent, eg, calcium, cations.

Sodium and calcium pectates, pectic acid, and pectinic acid all occur in the solid state as right-handed helices. In solid pectinic acid, the polymer molecules pack so that the chains are parallel to each other; the pectates pack as corrugated sheets of antiparallel chains. Junction zones in pectinic acid (HM pectin plus sucrose) gels are believed to be formed by a columnar stacking of methyl ester groups to form cylindrical hydrophobic areas parallel to the helix axes. LM pectin *[9049-34-7]* gels only in the presence of divalent cations. Two models for the formation of junction zones in calcium pectate *[12672-40-1, 40022-66-0]* gels have been proposed. One suggests an aggregation of chains by a cross-linking of carboxylate groups with calcium ions to form a structure similar to that of the corrugated sheets of antiparallel helices (3–6 chains in an average junction zone) found in solid calcium pectate. The other is the "egg box" model used to describe the formation of calcium alginate *[9005-35-0]* gels.

Xanthan. Xanthan, known commercially as xanthan gum *[11138-66-2]*, has a main chain of (1 → 4)-linked β-D-glucopyranosyl units; therefore, the chemical structure of the main chain is identical to the structure of cellulose *[9004-34-6]*. However, in xanthan, every other β-D-glucopyranosyl unit in the main chain is substituted on O-3 with a trisaccharide unit. The trisaccharide side chain consists of (reading from the terminal, nonreducing end in towards the main chain) a β-D-mannopyranosyl unit linked (1 → 4) to a β-D-glucopyranosyluronic acid unit linked (1 → 2) to a 6-*O*-acetyl-α-D-mannopyranosyl unit. About half of the terminal β-D-mannopyranosyl units carry a pyruvic acid group as a 4,6-di-*O*-acetal. The molecular weight is probably on the order of 2×10^6 daltons, although much higher figures have been reported.

The unusual properties of xanthan undoubtedly result from its structural rigidity, which in turn is a consequence of its linear, cellulosic backbone that is stiffened and shielded by the trisaccharide side chains. The conformation of xanthan in solution is a matter of debate. It does appear that the conformation changes with conditions.

Xanthan is the extracellular (exocellular) polysaccharide produced by *Xanthomonas campestris*. As with other microbial polysaccharides, the characteristics (polymer structure, molecular weight, solution properties) of xanthan preparations are constant and reproducible when a particular strain of the organism is grown under specified conditions, as is done commercially. The characteristics vary, however, with variations in the strain of the organism, the sources of nitrogen and carbon, degree of medium oxygenation, temperature, pH, and concentrations of various mineral elements.

Xanthan solutions are extremely pseudoplastic and have high yield values. These properties make xanthan almost ideal for the stabilization of aqueous dispersions, suspensions, and emulsions. Whereas other polysaccharide solutions decrease in viscosity when they are heated, xanthan solutions containing a small amount of salt (0.1% o) change little in viscosity over the temperature range 0–95°C. Although xanthan is anionic, pH has almost no effect on the viscosity of its solutions over the range pH 1–12. A synergistic viscosity increase results from the interaction of xanthan with galactomannans and with methylcellulose. The xanthan locust bean gum combination forms a thermally reversible gel when a solution of these two polysaccharides is heated and subsequently cooled.

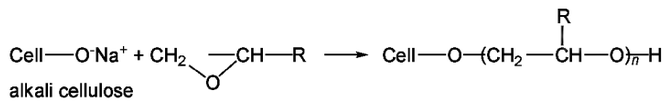
Cellulose Derivatives. Cellulose can be derivatized to make both water-soluble gums and hydrophobic polymers. The preparation of the hydrophobic cellulose esters (qv), cellulose acetates and cellulose nitrates, has already been mentioned. The water-soluble cellulose derivatives are cellulose ethers (qv).

Carboxymethylcelluloses (CMC). Carboxymethylcellulose *[9004-42-6]* (CMC) is the carboxymethyl ether of cellulose. To prepare CMC, cellulose is steeped in sodium hydroxide solution, and the so-called alkali cellulose is treated under controlled conditions with sodium monochloroacetate to form the sodium salt of carboxymethylcellulose and sodium chloride. Therefore, the CMC of commerce is actually sodium carboxymethylcellulose *[9004-32-4]*.

The physical properties (solution characteristics) of CMC, and all other linear polysaccharides, whether synthetic or natural, are determined by the average chain length or degree of polymerization (DP), the degree of substitution (DS), and the uniformity of substitution. The DS of different CMC types generally ranges from 0.4 to 0.8; some products may approach a DS of 1.5. The most widely used types have a DS of 0.7 or an average of 7 carboxymethyl groups per 10 β-D-glucopyranosyl units.

CMC hydrates rapidly and forms clear solutions. Viscosity building is the single most important property of CMC. Dilute solutions of CMC exhibit stable viscosity because each polymer chain is hydrated, extended, and independent. The sodium carboxylate groups are highly hydrated, and the cellulose molecule itself is hydrated. The cellulose molecule is linear, and conversion of it into a polyanion (polycarboxylate) tends to keep it in an extended form by reason of coulombic repulsion. This same coulombic repulsion between the carboxylate anions prevents aggregation of the polymer chains. Solutions of CMC are either pseudoplastic or thixotropic, depending on the type.

Hydroxyethyl- and Hydroxypropylcelluloses. Hydroxyalkylcelluloses are cellulose ethers prepared by reaction of alkali cellulose with ethylene oxide, to prepare hydroxyethylcellulose (HEC) *[9004-62-0]*, or propylene oxide, to prepare hydroxypropylcellulose (HPC) *[9004-64-2]*.



These products are characterized in terms of moles of substitution (MS) rather than DS. MS is used because the reaction of an ethylene oxide or propylene oxide molecule with cellulose leads to the formation of a new hydroxyl group with which another alkylene oxide molecule can react to form an oligomeric side chain. Therefore, theoretically, there is no limit to the moles of substituent that can be added to each D-glucopyranosyl unit. MS denotes the average number of moles of alkylene oxide that has reacted per D-glucopyranosyl unit. Because starch is usually derivatized to a considerably lesser degree than is cellulose, formation of substituent poly(alkylene oxide) chains does not usually occur when starch is hydroxyalkylated and DS MS.

In general, the MS controls the solubility of both HEC and HPC. For example, water-soluble grades of hydroxyethylcellulose have MS values of 1.6–3.0; those with MS 0.3–1.0 are soluble in aqueous alkali. Even higher MS types of hydroxypropylcellulose become soluble in organic solvents, first polar, then nonpolar solvents.

Clear, water-soluble, oil-and grease-resistant films of moderate strength can be cast from hydroxyethylcellulose solutions. Flexible, nontacky, heat-sealable packaging films and sheets can be produced from hydroxypropylcellulose by conventional extrusion techniques. Both gums can be used in the formulation of coatings, and both can be used to form edible films and coatings.

Methylcelluloses and Hydroxyalkylmethylcelluloses. Methylcellulose *[9004-67-5]* contains methoxyl groups in place of some of the hydroxyl groups along the cellulose molecule. The primary hydroxyl group of cellulose is somewhat more reactive so, as with other cellulose derivatives, there is a somewhat higher degree of substitution at O-6. The next most acidic hydroxyl group is O-2. Hydroxyalkylmethylcelluloses contain, in addition to methoxyl groups, hydroxyalkoxyl groups in place of some of the hydroxyl groups. As with all other polysaccharide derivatives, the properties of methyl- and hydroxyalkylmethylcelluloses are a function of the type(s) of derivatization, the amount of each type of substituent group, the molecular weight distribution, and to some extent, the physical nature of the product, eg, fibrous vs powdered, granulation size, and surface treatment. Because these variables can be controlled to some degree, the members of this family, generally referred to simply as methylcellulose, are a group of tailor-made products, as are other starch and cellulose derivatives.

Methylcellulose is made by reaction of alkali cellulose with methyl chloride until the DS reaches 1.1–2.2. Hydroxypropylmethylcellulose *[9004-65-3]*, the most common of this family of products, is made by using propylene oxide in addition to methyl chloride in the reaction; MS values of the hydroxypropyl group in commercial products are 0.02–0.3. Use of 1,2-butylene oxide in the alkylation reaction mixture gives hydroxybutylmethylcellulose *[9041-56-9, 37228-15-2]* (MS 0.04–0.11). Hydroxyethylmethylcellulose *[9032-42-2]* is made with ethylene oxide in the reaction mixture.

Conversion of some of the hydroxyl groups of cellulose molecules into methyl ether groups increases the water solubility of the cellulose molecule and reduces its ability to aggregate, ie, reduces intermolecular interactions. Solubility is increased even more when hydroxyalkyl groups are added to methylcellulose. Solutions of all these products behave somewhat like those of guar and locust bean gums, ie, as linear polysaccharides with short side chains that give stable solutions of high viscosity. As substituent groups are added, the solubility of the products changes from insoluble to soluble in aqueous alkali, to soluble in water, to soluble in various polar organic solvents, such as water–alcohol solutions, alcohols, and alcohol–hydrocarbon solutions.

The most interesting property of these nonionic products is thermal gelation. Solutions of members of this family of gums that are soluble in cold water, like solutions of other polysaccharides, decrease in viscosity when heated. However, unlike other gums, when a certain temperature is reached, depending on the specific product, the solution viscosity increases rapidly and the solution gels. Gelation can occur from ~45° to ~90°C, depending on the type. The thermal gelation is reversible.

Methylcellulose reduces surface and interfacial tension. Methylcellulose forms high strength films and sheets that are clear, water-soluble, and oil- and grease-resistant, and have low oxygen and moisture vapor transmission rates (see BARRIER POLYMERS).

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CARBON

Carbon and artificial graphite,
Activated carbon,
Carbon black,
Diamond, natural,
Diamond, synthetic,
Natural graphite,

CARBON AND ARTIFICIAL GRAPHITE

Structure, terminology, and history,
Baked and graphitized carbon,
Processing of baked and graphitized carbon,
Properties of manufactured graphite,
Applications of baked and graphitized carbon,
Other forms of carbon and graphite,

STRUCTURE, TERMINOLOGY, AND HISTORY

Elemental carbon *[7440-44-0]*, atomic number six in the periodic table, at wt 12.011, occurs naturally throughout the world in either its crystalline, more ordered, or amorphous, less ordered, form. Carbonaceous materials such as soot or charcoal are examples of the amorphous form whereas graphite and diamond are crystalline. Carbon atoms bond with other carbon atoms as well as with other elements, principally hydrogen, nitrogen, oxygen, and sulfur, to form carbon compounds, which are the subject of organic chemistry. The manufactured form of carbon and graphite is discussed within this article. In its many varying manufactured forms, carbon and graphite can exhibit a wide range of electrical, thermal, and chemical properties that are controlled by the selection of raw materials and thermal processing during manufacture (1).

Crystallographic Structure

There are two allotropes of carbon: diamond *[7782-40-3]* and graphite *[7782-42-5]*. The diamond, or isotropic form, has a crystal structure that is face-centered cubic with interatomic distances of 0.154 nm. Each atom is covalently bonded to four other carbon atoms in the form of a tetrahedron. The nature of the bonding explains the differences in properties of the two allotropic forms. The hardness of diamond is derived from the regular three-dimensional network of σ-bonds; the low electrical conductivity results from fixed-bonding electrons between atoms within the diamond lattice (2). Graphite, or the anisotropic form, has a structure that is composed of infinite layers of carbon atoms arranged in the form of hexagons lying in planes. This structure was first proposed in 1924 (3). The stacking arrangement is ABAB with atoms in alternate planes aligning with each other. Interlayer spacing is 0.3354 nm and interatomic distance within the planes 0.1415 nm. The crystal density is 2.25 g cm^3 compared to 3.51 g cm^3 for diamond.

A rhombohedral form, which occurs in small proportions with the hexagonal form, has a stacking arrangement of ABCABC. Being less stable, it begins to convert to the hexagonal form above 1300°C (4).

In 1990, a third form of solid carbon was confirmed and designated "buckminsterfullerenes." These 60-carbon (and 78-C) clusters are described as having the shape of a geodesic dome or soccer ball and hence are also known as "bucky balls" (5).

The electronic ground state of carbon is $1s^2$, $2s^2$, $2p^2$, ie, there are four electrons in the outer shell available for chemical bonding. In diamond, the 2*s* and 2*p* electrons mix to form four equivalent covalent σ-bonds. In graphite, three of the four electrons form strong covalent π-bonds with the adjacent in-plane carbon atoms. The fourth electron forms a less strong bond of the van der Waals type between the planes. Bond energy between planes is 17 kJ mol (4 kcal mol) (6) and within planes 477 kJ mol (114 kcal mol) (7). The weak forces between planes account for such properties of graphite as good lubricity and the ability to form interstitial compounds, whereas the strong π-bonding within the planes contributes to the high electrical and thermal conductivity.

Terminology

A wide variety and range of bulk carbon forms are available within the industry. In general, commercial forms are loosely characterized as carbon or graphite, but they are distinctly different. In the United States, the ASTM has issued definitions of terms that relate to manufactured carbon and graphite including processing and property definitions (8). The term manufactured carbon (sometimes called formed carbon, amorphous carbon, or baked carbon) refers to a bonded granular carbon body whose matrix has been subjected to a temperature typically between 900 and 2400°C (8). The process involves mixing carbonaceous filler materials, such as petroleum coke, carbon blacks, or anthracite coal, with binder materials of coal tar or petroleum pitch, forming these mixtures by molding or extrusion, and baking the mixtures in furnaces at temperatures from 900 to 2400°C. Green carbon refers to formed carbonaceous material that has not been baked.

Manufactured graphite (sometimes called synthetic, artificial graphite, electrographite, or graphitized carbon) refers to a bonded granular carbon body whose matrix has been subjected to a temperature typically in excess of 2400°C and whose matrix is thermally stable below that temperature (8). This higher temperature processing, known as graphitization (see PROCESSING OF BAKED AND GRAPHITIZED CARBON) changes not only the crystallographic structure but the physical and chemical properties as well.

Pyrolytic carbons are carbon materials deposited on a heated graphite substrate, or other material, by chemical vapor deposition (CVD) at 800–2300°C; pyrolytic graphite is the product that results from higher temperature treatment and has a crystallite interlayer spacing similar to that of ideal graphite (9). Carbon or graphite fiber forms are produced principally from polyacrylonitrile (PAN) or pitch and are designated carbon or graphite based on crystallographic structure (see CARBON AND GRAPHITE FIBERS).

Whereas the foregoing are the forms most commonly found in many applications in industry, there are definitions that are necessary not only for industrial purposes but also for consistency in the study of carbon science. Since 1975, the International Committee for Characterization and Terminology of Carbon has been working to establish definitions and in 1982 published its 30 tentative definitions followed by periodic issues of further tentative definitions (10).

History of the Industry

Natural graphite has been known since the Middle Ages for its use in making clay–graphite crucibles and for its lubricating properties. The first known use was for drawing or writing, and it was because of this attribute that the German mineralogist, A. G. Gerner, named graphite after the greek word "graphein" which means to write (11) (see CARBON, NATURAL GRAPHITE).

Manufacture of artificial graphite did not come about until the end of the nineteenth century. Its manufacture was preceded by developments mainly in the fabrication and processing of carbon electrodes. H. Davy is credited with using the first fabricated carbon in his experiments on the electric arc in the early 1800s. During the nineteenth century, several researchers received patents on various improvements in carbon electrodes. The invention of the dynamo and its application to electric current production in 1875 in Cleveland, Ohio, by C. F. Brush, provided a market for carbon products in the form of arc-carbons for street lighting. The work of a Frenchman, F. Carre, in the late nineteenth century, established the industrial processes of mixing, forming, and baking necessary for the production of carbon and graphite (12).

A significant development occurred when E. G. Acheson patented an electric resistance furnace capable of reaching approximately 3000°C, the temperature necessary for graphitization (13). This development was the beginning of a new industry in which improved carbon and graphite products were used in the production of alkalies, chlorine, aluminum, calcium and silicon carbide, and for electric furnace production of steel and ferroalloys. In 1942, a new application for graphite was found when it was used as a moderator by E. Fermi in the first self-sustaining nuclear chain reaction (14). This nuclear application and subsequent use in the developing aerospace industries opened new fields of research and new markets for carbon and graphite. Carbon and graphite fibers and their use in composite materials are examples of a new form and a new industry.

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BAKED AND GRAPHITIZED CARBON

Raw Materials

The raw materials used in the production of manufactured carbon and graphite largely control the ultimate properties and practical applications of the final product. This dependence is related to the chemical and physical nature of the carbonization and graphitization processes.

Essentially any organic material can be thermally transformed to carbon. The carbonization process through the elimination of heteroatoms and substituent hydrogen converts the organic precursor into a carbon polymer. This polymer consists of aromatic carbons arranged in large polynuclear aromatic ring systems. With continued heat treatment, this carbon is transformed to a more or less ordered three-dimensional framework approaching the structure of graphite. Differences in the final material depend on the ease and extent of completion of these overall chemical and physical ordering processes.

In most carbon and graphite processes, the initial polymerization reactions occur in the liquid state. The subsequent stages of crystal growth, heteroatom elimination, and molecular ordering occur in the solid phase. The result is the development of a three-dimensional graphite structure.

Most of the raw materials in the production of bulk carbon and graphite products are derived from petroleum (qv) and coal (qv). These precursors are generally residual by-products and exhibit a highly aromatic composition. The two main raw materials for carbon and graphite are pitches and cokes. Pitches are derived from distillation and thermal heat treatment of tars or oils. Pitches are solid at room temperature but soften to a liquid at elevated temperatures. As a result of thermal processing, commercial pitches are extremely complex materials with literally hundreds to thousands of discrete molecular components. These components are predominantly polynuclear aromatic or heterocyclic species with varying degrees of alkyl group substitution. Pitches have a glasslike character, generally exhibit a glass-transition temperature, and soften over a very broad temperature range. The melting temperatures and temperature–viscosity behavior of pitches vary with their processing conditions. Conventional petroleum and coal-derived pitches have average molecular weights of 300–500 and structures containing on the order of 3–12 aromatic rings.

Pitches can be transformed to a mesophase state by further chemical and physical operations. Heat treatment of conventional pitches results in additional aromatic polymerization and the distillation of low molecular weight components. This results in an increase in size and concentration of large planar aromatic molecular species whereupon the precursor pitch is transformed to a mesophase state exhibiting the characteristics of nematic liquid crystals (1). Additional heat treatment converts the mesophase pitch to an infusible aromatic hydrocarbon polymer designated as coke.

Cokes are infusible solids with average molecular weights estimated to be on the order of several thousand. Coke can be described as a thermoset aromatic hydrocarbon polymer. The molecular order and structure of coke is determined by the chemical and physical processes that occur in the liquid mesophase state. Subsequent high temperature heat treatment of coke, as in calcination, induces solid-state polymerization and ordering while removing substituent atoms in the form of gaseous by-products. Sulfur and nitrogen, present in the coke precursor, can be stabilized and incorporated into the aromatic polymer structure at this stage. These heteroatoms evolve rapidly during graphitization by a phenomenon designating as puffing.

Bulk carbon and graphite products, such as electrodes, are produced using calcined coke as a filler and liquid pitch as a binder. After mixing, the blend is molded or extruded to a desired shape and then baked and graphitized to produce the final carbon or graphite product. Although many different raw materials are used in the manufacture of carbon and graphite, the primary materials in terms of total tonnage are calcined petroleum coke used as a filler material and coal-tar pitch as a binder. Petroleum and coal-tar pitches are also utilized as impregnants to strengthen the final graphite artifact. Coal-tar-based coke and anthracite coal are also widely employed as filler materials for carbon and graphite.

High carbon yielding resins are sometimes employed as raw material precursors for specialty carbons. Various chemical additives are also used in low concentrations to improve the processability or to control puffing during graphitization.

Filler Materials.

Petroleum Coke. Petroleum coke is the largest single precursor material in terms of quantity for manufactured carbon and graphite products. Commercial coke is produced by the delayed coking of heavy petroleum by-products. Delayed coking technology is currently practiced throughout the world. Delayed coke can fall into several categories: fuel-grade, aluminum-grade, and coke for carbon and graphite. The coke employed for carbon and graphite includes regular coke and needle coke. Needle or premium coke is used in the production of graphite electrodes for electric arc furnaces whereas regular coke is used for other carbon and graphite products.

The key difference in the production of regular and needle petroleum coke is the feedstock precursor. Needle coke is generally produced from highly aromatic starting materials such as decant oil derived from catalytic cracking of petroleum distillate. Before it is fed to the delayed coker, the decant oil can be pretreated by a hydrodesulfurization (HDS) process to remove sulfur or thermally cracked to a thermal tar to increase carbon yield. Regular and aluminum-grade cokes are generally prepared from the residues (resids) of crude oil distillation. Pyrolysis tars from naphtha or gas-oil cracking can also be employed to produce intermediate-grade cokes, which exhibit more or less needlelike character depending on the tar composition and coke preparation parameters.

Although the feedstock exerts the greatest influence, coke properties are also determined by process variables including coking time and temperature, pressure, and recycle ratio. The most important properties in delayed coke are sulfur level, volatile matter content, ash, coefficient of thermal expansion (CTE), and hardness. The CTE, which is generally measured on an extruded graphite artifact prepared using the coke as a filler, reflects the needlelike character of the coke. Premium cokes for graphite electrodes are anisotropic and have very low CTEs in the extrusion direction. Regular cokes are isotropic and give graphite artifacts with high CTE values.

The sulfur level of cokes is important from an environmental standpoint since sulfur is released during eventual graphitization of the coke-based product. High sulfur cokes also lead to irreversible rapid expansion, puffing, of the synthetic carbon during the graphitization process. Excessive puffing results in lower strength and density and can cause cracks and splits in the graphitized artifact. A high volatile content in the raw coke leads to a degradation in coke density and strength during subsequent calcining. A high ash content is usually undesirable and leads to contamination in the finished product. High ash is particularly detrimental for needle coke feedstock since the ash particles interfere with the coalescence of the mesophase and the development of long-range order and anisotropy. The raw coke must be sufficiently hard to prevent excessive degradation into fines during subsequent calcination.

The selection of petroleum coke for a particular graphite product is based on the combination of these properties. For a premium needle coke, a decant oil feedstock is usually selected or pretreated to give a coke that is low in sulfur, low in ash, and exhibits a low coefficient of thermal expansion. When evaluated as fillers in graphitized artifacts, these cokes give CTE values $<0.3 \times 10^{-6}$ °C between 25–100°C. Tars derived from the thermal cracking of gas oils and certain pyrolysis tars can also give needlelike cokes with appropriate processing. A necessary requirement for these feedstocks is that they develop a highly ordered mesophase with large anisotropic domains. During coking, the mesophase is oriented by the gaseous volatiles and shear forces to give the aligned needle coke structure (2).

Cokes derived from resids or blends of resids with other petroleum feedstocks give high CTE values and are utilized as fillers for aluminum anodes and certain specialty carbon and graphite products. The remaining properties differ depending on the final application. A low ash content is required for

cokes used in the aluminum industry since these impurities tend to concentrate in the aluminum as the anode is consumed. Impurities that are of particular concern include: vanadium, nickel, iron, and silicon; other impurities such as sulfur are slightly less critical. Since the carbon consumption per kilogram of aluminum produced affects the economics of the process, bulk density and oxidation resistance are also important properties.

Low sulfur and ash levels are required for high CTE, isotropic cokes used for carbon and graphite specialty products. Highly isotropic cokes are also the filler materials for producing graphite for nuclear reactors. The purity, particularly the boron content, is critical in this application. Properties of typical needle and isotropic (regular) cokes are summarized in Table 1.

Table 1. Typical Properties of Isotropic and Needle Cokes[a]

Property	Aluminum anode-grade coke		Graphite electrode-grade needle coke	
	Raw	Calcined[b]	Raw	Calcined[b]
sulfur, wt %	2.5	2.5	0.8	0.8
ash, wt %	0.25	0.30	0.10	0.15
vanadium, ppm	150	200	10	10
nickel, ppm	150	200		20–40
silicon, wt %	0.02	0.02	0.04	0.04
volatile matter, wt %	10–12		8	
resistivity, $\mu\Omega\cdot m$		950		1100
real density, g/cm^3		2.06		2.12
bulk density, g/cm^3		0.80		0.88
coefficient of thermal expansion of graphite per °C (25–100°C)		2×10^{-6}		0.3×10^{-6}

[a] Revised data based on Ref. 3.

[b] Calcining, discussed later in this section, is a thermal treatment that removes volatiles from the raw materials and shrinks the particles.

Coal-Tar Pitch Coke. Coal-tar pitch is used to produce needle coke primarily in Japan. Processes for producing needle coke from pitch have also been developed in Germany (4). The key to producing needle coke from coal tar or coal-tar pitch is the removal of the high concentrations of infusible solids, or material insoluble in quinoline (QI), which are present in the original tar. The QI inhibits the growth of mesophase and results in an isotropic, high CTE coke from coal-tar pitch. After removal of the QI, very anisotropic and low CTE cokes are obtained from coal-tar-based materials.

Because of very high aromaticity, high coking value, and excellent coking characteristics, coal tar and coal-tar pitches are very attractive premium coke precursors. The solids removal prior to coking is usually accomplished through filtration with the use of a cosolvent (5). Transformation to coke may employ different technology from conventional delaying coking. Since coal-tar materials contain substantial quantities of heterocyclic nitrogen, puffing can be a problem during rapid graphitization.

Natural Graphite. Natural graphite is a crystalline mineral form of graphite occurring in many parts of the world (see CARBON NATURAL GRAPHITE). It is occasionally used as a component in carbon and graphite production. Intercalated natural graphite is used to form a flexible graphite product, such as GRAFOIL brand flexible graphite, which is utilized for gasket and sealing applications. GRAFOIL is a registered trademark of UCAR Carbon Technology Corp.

Carbon Blacks. Carbon blacks are occasionally used as components in mixes to make various types of carbon products. Carbon blacks are generally prepared by deposition from the vapor phase using petroleum distillate or gaseous hydrocarbon feedstocks (see CARBON, CARBON BLACK).

Anthracite. Anthracite is preferred to other forms of coal (qv) in the manufacture of carbon products because of its high carbon-to-hydrogen ratio, its low volatile content, and its more ordered structure. It is commonly added to carbon mixes used for fabricating metallurgical carbon products to improve specific properties and reduce cost. Anthracite is used in mix compositions for producing carbon electrodes, structural brick, blocks for cathodes in aluminum manufacture, and in carbon blocks and brick used for blast furnace linings.

Synthetic Resins. Various polymers and resins are utilized to produce some specialty carbon products such as glassy carbon or carbon foam and as treatments for carbon products. Typical resins include phenolics, furan-based polymers, and polyurethanes. These materials give good yields of carbon on pyrolysis and generally carbonize directly from the thermoset polymer state. Because they form little or no mesophase, the ultimate carbon end product is nongraphitizing.

Binders.

Pitches. Carbon articles are made by mixing a controlled size distribution of coke filler particles with a binder such as coal-tar or petroleum pitch. The mix is then formed by molding or extruding and is heated in a packed container to control the shape and set the binder. Thus the second most important raw material for making a carbon article is the pitch binder. The pitch binder preserves the shape of the green carbon and also fluidizes the carbon particles, enabling them to flow into an ordered alignment during the forming process. During the subsequent baking steps, the pitch binder is pyrolyzed to form a coke that bridges the filler particles and serves as the permanent binding material. These carbon bridges provide the strength in the finished article and also provide the paths for energy flow through thermal and electric conductance.

A binder used in the manufacture of electrodes and other carbon and graphite products must: (*1*) have high carbon yield, usually 40–60 wt % of the pitch; (*2*) show good wetting and adhesion properties to bind the coke filler together; (*3*) exhibit acceptable softening behavior at forming and mixing temperature, usually in the range of 90–180°C; (*4*) be low in cost and widely available; (*5*) contain only a minor amount of ash and extraneous matter that could reduce strength and other important physical properties; and (*6*) produce binder coke that can be graphitized to improve the electrical and thermal properties.

The principal binder material, coal-tar pitch, is produced by the distillation of coal tar. Coal tar is obtained primarily as a by-product of the destructive distillation of bituminous coal in coke ovens during the production of metallurgical coke. Petroleum pitch is used to a much lesser extent as a binder in carbon and graphite manufacture. Because of its low solids content, petroleum pitch is used as an impregnant to strengthen carbon artifacts prior to graphitization.

Pitches are characterized by softening point, carbon yield, solubility in aromatic solvents such as toluene and quinoline, ash, and heteroatom content. Since pitches soften over a broad temperature range, arbitrary methods have been used to define pitch softening point. The Mettler method, ASTM D3104, has been adopted as a standard procedure in the United States. For binder pitches, both the softening point and the viscosity versus temperature behavior are important in determining the forming conditions of the carbon and graphite product. For impregnation, the viscosity temperature dependence controls the impregnation temperature.

Coal-tar binder pitches differ both chemically and constitutionally from petroleum pitches (Table 2). The coal-tar pitches are composed primarily of unsubstituted polynuclear aromatic hydrocarbons and heterocyclics. Substantial quantities of nitrogen-containing compounds, and to a lesser extent sulfur heterocyclics, are present in coal-tar pitch. Coal-tar pitches generally contain substantial quantities of QI. The QI is largely an infusible low temperature carbonaceous solid produced in the coking operation used to generate the precursor tar. Some coal particles and mesophase can also be included in the QI. The QI contributes to the carbon yield of the binder and serves to strengthen the carbon artifact. Excessive amounts of QI adversely affect the rheology of the pitch binder.

Table 2. Properties of Petroleum Impregnating and Coal-Tar Binder Pitches

Property	Petroleum	Coal tar
Mettler softening point, °C	120	110
sp gr 25°C, g/mL	1.24	1.33
coking value, wt %	51	60
toluene insolubles (TI), wt %	3.6	33
quinoline insolubles (QI), wt %	0.2	14
ash, wt %	0.16	0.10
sulfur, wt %	3.0	0.8
nitrogen, wt %	0.3	1.0
viscosity in Pa·s[a]		
150°C	15.0	3.6
160°C	4.5	1.5
170°C	1.7	0.8
aromatic H, %	60	90
average molecular weight	500	350

[a] To convert Pa·s to poise, multiply by 10.

Coal-tar binder pitches are produced with varying softening points depending on the application and the carbon–graphite manufacturing process. Typical softening points for binder pitches used in manufacture of graphite electrodes range from about 90–120°C. Higher and lower softening point pitches are used in specialty applications. Coal-tar impregnating pitches with little or no QI are used in Japan and Europe. In Japan, QI removal procedures similar to those used for producing pitch coke are employed. The production and usage of coal-tar pitches as binders for carbon and graphite have been reviewed (6).

In North America, petroleum pitch is used primarily as a carbon impregnating material. The petroleum pitch is prepared by the thermal cracking and distillation of decant oil. The components of petroleum pitch are largely alkyl substituted polynuclear aromatics and heterocyclics. The latter are predominantly sulfur compounds. Unlike coal-tar pitches, petroleum pitches have very low QI contents. The solids in petroleum pitch are mainly catalyst fines that were present in the original decant oil. The principal commercial petroleum impregnant pitch has a Mettler softening point of about 120°C. However, petroleum pitches with softening points as high as 280°C are available for use in certain specialty applications.

Certain compounds found in some coal-tar and petroleum pitches are carcinogenic. Individuals working with pitches or exposed to fumes or dust should wear protective clothing to avoid skin contact. Respirators should be worn when pitch dust or fume concentrations in the air are above established limits.

Additives. In addition to the primary ingredients, the fillers and binders, minor amounts of other materials are added at various steps in the carbon and graphite manufacturing process. Although the amounts of these additives are usually small, they can play an important role in determining the quality of the final product. Light extrusion oils and lubricants, including petroleum oils, waxes, fatty acids, and esters, are often added to the mix to improve the extrusion rates and structure of the extruded products. Chemical inhibitors are introduced to reduce the detrimental effects of sulfur in high sulfur cokes. Iron oxide is often added to high sulfur coke to prevent puffing, the rapid swelling of the coke caused by volatilization of the sulfur at 1600–2400°C. The iron from Fe_2O_3 or other iron compounds prevents this action by forming a more stable iron sulfide, which reduces the gas pressure in the coke particles (7). Other sulfide-forming compounds such as those from sodium, nickel, cobalt, and vanadium may also be used.

Calcining

Nearly all raw coke utilized in carbon manufacture is calcined. Calcination consists of heating raw coke to remove volatiles and to shrink the coke to produce a strong, dense particle. Raw petroleum coke, eg, has 5–15% volatile matter. When the coke is calcined to 1400°C, it shrinks approximately 10–14%. Less than 0.5% of volatile matter in the form of hydrocarbons remains in raw coke after it is calcined to 1200–1400°C. During calcination, the evolving volatiles are primarily methane and hydrogen, which burn during the calcining process to provide much of the heat required. The calcining step is particularly important for those materials used in the manufacture of graphite products, such as electrodes, since the high shrinkages occurring in raw coke during the baking cycle of large electrodes would cause the electrode to crack. To prevent partial fusion of the coke during calcining, the volatile content of the green coke is kept below 12%. The real density of coke increases during calcining from about 1.3 g/mL to 2.0–2.2 g/mL.

Anthracite is calcined at appreciably higher temperatures (1800–2000°C). The higher calcining temperatures for anthracite are necessary to complete most of the shrinkage and to increase the electrical conductivity of the product for use in either Soderberg or prebaked carbon electrodes for aluminum, silicon, or phosphorus manufacture.

The selection of calcining equipment depends on the temperatures required and the materials to be calcined. There are two principal types of coke calcining units in operation utilizing either kilns or hearths.

A calcining kiln is a horizontal steel cylinder, slightly sloped to help the coke move forward and lined with refractory brick. The raw coke is fed at the upper end, natural gas or oil is burned at the lower end, and the combustion gas flows through the kiln above and against the coke stream.

The rotary hearth is a horizontal plate, which is lined with refractory and turns at a slow rate. The coke enters at the perimeter and moves toward the center. Natural gas is fired around the circumference of the dome and the hot coke drops through a central pit into a rotary cooler.

The yield of coke calcined in a kiln is usually slightly above 80% of the dry raw coke. Higher yields are achieved in rotary hearths because very little of the fines are burned or carried away by the combustion gas.

Since anthracite must be calcined at higher temperatures than can be reasonably attained in conventional gas-fired kilns, an electrically heated shaft kiln is used to calcine coal at temperatures up to 2000°C (8).

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PROCESSING OF BAKED AND GRAPHITIZED CARBON

Raw Material Preparation

Crushing and Sizing. Calcined petroleum coke arrives at the graphite manufacturer's plant in particle sizes ranging typically from dust to 50–80 mm diameter. In the first step of artificial graphite production, the run-of-kiln coke is crushed, sized, and milled to prepare it for the subsequent processing steps. The degree to which the coke is broken down depends on the grade of graphite to be made. If the product is to be a fine-grained variety for use in aerospace, metallurgical, or nuclear applications, the milling and pulverizing operations are used to produce sizes as small as a few micrometers in diameter. If, on the other hand, the product is to be coarse in character for products like graphite electrodes used in the manufacture of steel, a high yield of particles up to 25 mm diameter is necessary.

The wide variety of equipment available for the crushing and sizing operations is well described in the literature (1,2). Roll crushers are commonly used to reduce the incoming coke to particles that are classified in a screening operation. The crushed coke fraction, smaller than the smallest particle needed, is normally fed to a roll or hammer mill for further size reduction to the very fine (flour) portion of the carbon mix. A common flour sizing used in the graphite industry contains particles ranging from 149 μm (100 mesh) to a few micrometers with about 50% passing through a 74 μm (200 mesh) screen.

For a coarse-grained (particle containing) graphite, the system depicted in Figure 1 is typical. The run-of-kiln coke is brought in on railroad cars and emptied into pits where the coke is conveyed to an elevator. The elevator feeds a second conveyor that empties the coke into any one of a number of storage silos where the coke is kept dry. The manufacturer usually specifies a maximum moisture content in the incoming coke at about 0.1–0.2% to ensure that mix compositions are not altered by fluctuations in moisture content.

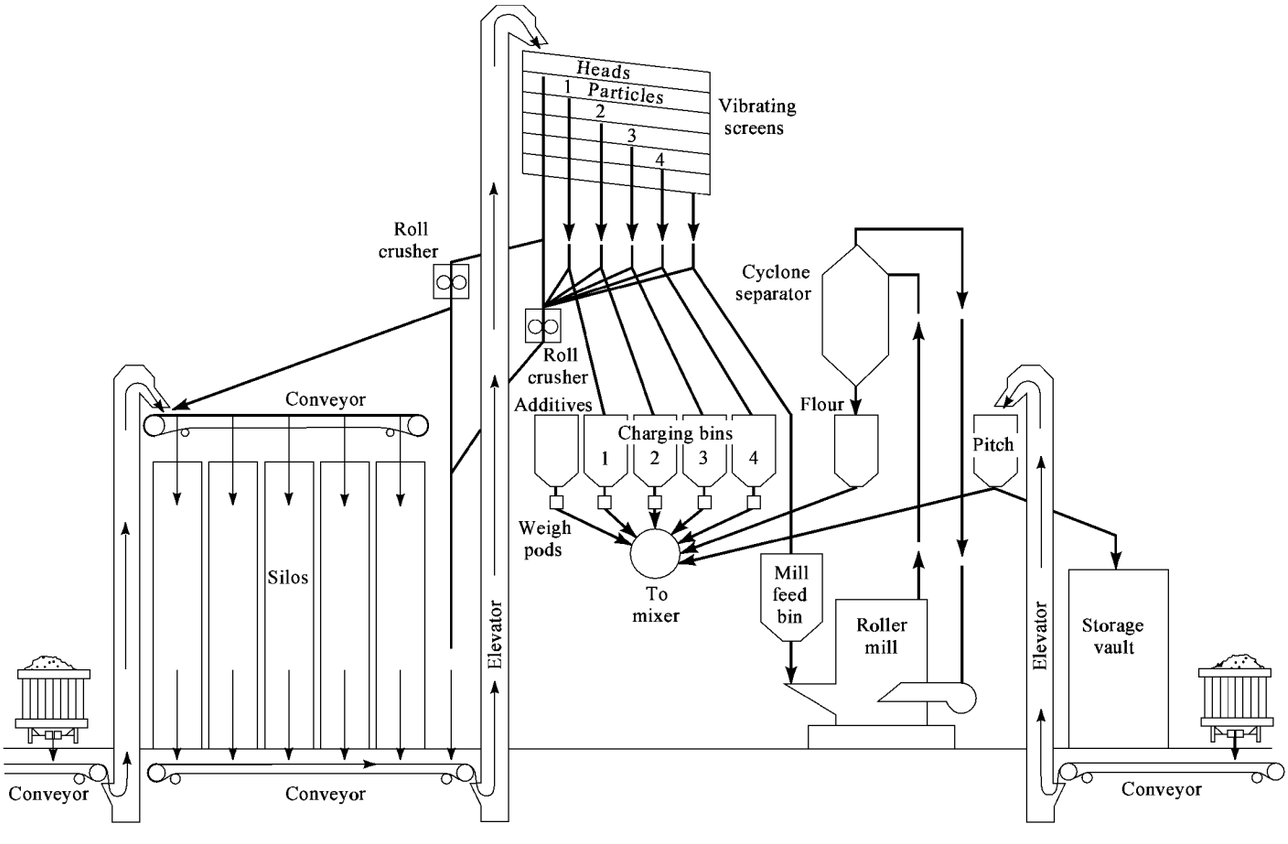

Fig. 1. Raw materials handling system.

Courtesy of UCAR Carbon Technology Corp.

In the system shown in Figure 1 the oversized coke particles (heads) are diverted to a roll crusher. Most raw material systems provide the option of further reducing the sizes of particles by passing them through a second crusher directly from the screens and recycling the resulting fractions through the screening system. The undersized coke fractions are transferred to a bin that supplies a mill for production of the flour portion of graphite composition. The mills used in this application may be of impact (hammer) variety or of roller variety. A commonly used mill consists of a rotating roller operating against a stationary steel ring. The coke is crushed to very fine sizes that are air-classified by a cyclone separator. The sizes larger than those desired in the flour are returned to the mill and the acceptable sizes are fed to a charge bin.

The coal-tar pitch binder used in graphite manufacture also arrives in railroad cars. If the pitch is shipped in bulk form, the large pieces must be crushed to ca 30 mm and smaller to facilitate uniform melting in the mixer and control of the weighing operation. Many vendors of binder pitches now form their product either by prilling, extruding, or flaking to ensure ease of handling and storage.

The pitch system shown in Figure 1 conveys the incoming pitch through a crusher to an elevator that deposits it into a charging bin. The graphite manufacturer tries to avoid long-term storage of 100°C softening point pitch because of its tendency to congeal at ambient conditions into masses extremely difficult to break up and handle. Thus, whenever possible, cars of pitch are ordered and used as needed at the carbon plant.

In some plants the pitches are received and stored as liquids. Addition to the mixers can be either through a weighing system or positive displacement pumps (3). Except for equipment differences, the results of utilizing liquid pitch are similar to bulk.

Proportioning. The size of the largest particle is generally set by application requirements. For example, if a smoothly machined surface with a minimum of pits is required, as in the case of graphites used in molds, a fine-grained mix containing particles no larger than 1.6 mm with a high flour content is ordinarily used. If high resistance to thermal shock is necessary, eg, in graphite electrodes used in melting and reducing operations in steel plants, particles up to 25 mm are used to act as stress absorbers in preventing catastrophic failures in the electrode.

Generally, the guiding principle in designing carbon mixes is the selection of the particle sizes, the flour content, and their relative proportions in such a way that the intergranular void space is minimized. If this condition is met, the volume remaining for binder pitch and the volatile matter generated in baking are also minimized. Volatile evolution is often responsible for structural and property deterioration in the graphite product. In practice, most carbon mixes are developed empirically with the aim of minimizing binder demand and making use of all the coke passed through the first step of the system. From an economic standpoint, accumulation of one size component cannot be tolerated in making mixes for commonly used graphite grades since this procedure amounts to a loss of relatively costly petroleum coke. Typically, a coarse-grained mix may contain a large particle, eg, 13 m diameter, two to three intermediate particle sizes, and flour. In this formulation approximately 25 kg of binder pitch would be used for each 100 kg of coke.

Although binder levels increase as particle size is reduced, and they are greatest in all-flour mixes where surface area is very high, the principle of minimum binder level still applies. The application of particle packing theory to achieve minimum binder level in all-flour mixes is somewhat more complex because of the continuous gradation in sizes encountered (4).

For some carbon and graphite grades, particle packing and minimum pitch concepts are not used in arriving at a suitable mix design. For relatively small products, eg, where large dimensional changes can be tolerated during the baking and graphitizing operations, high binder contents are often used. Increased pitch content results in greater shrinkage, which gives rise to high density and strength in the finished products.

Mixing. Once the raw materials have been crushed, sized, and stored in charging bins and the desired proportions established, the manufacturing process begins with the mixing operation. The purpose of mixing is to blend the coke filler materials and distribute the pitch binder over the surfaces of the filler grains as it melts or is added as a liquid. The intergranular bond ultimately determines the properties and structural integrity of the graphite. Thus the more uniform the binder distribution is throughout the filler components, the greater the likelihood for a structurally sound product.

The degree to which mixing uniformity is accomplished depends on factors such as time, temperature, and batch size. However, a primary consideration in achieving mix uniformity is mix design (see MIXING AND BLENDING). A number of mechanically agitated, indirectly heated mixer types are available for this purpose (5,6). Each mixer type operates with a different mixing action and intensity. Ideally, the mixer best suited for a particular mix composition is one that introduces the most work per unit weight of mix without particle breakdown. In practice, only a few mixer types are used in graphite manufacture.

The cylinder mixer is commonly used for coarse-grained mixes. It is equipped with an axial rotating shaft fitted with several radial arms where paddles are attached. The intensity of this mixer is relatively low to avoid particle breakdown and long mixing times, such as 90 min, are therefore needed to complete the mixing operation. With fine-grained compositions, more intensive mixers may be used with a corresponding reduction in mixing time. Bread or sigma-blade mixers and the high intensity twin-screw mixers of the Werner-Pfleiderer and Banbury variety are examples of the equipment that can be used on fine-grained compositions. For both mixers temperatures at the time of discharge are 160–170°C.

Following the mixing operation, the hot mix must be cooled to a temperature slightly above the softening point of the binder pitch. Thus the mix achieves the proper rheological consistency for the forming operation and the formed article is able to maintain its shape better as it cools to room temperature. At the end of the cooling cycle, which typically requires 15–30 min, the mix is at 100–110°C and is ready to be charged into an extrusion press or mold.

Forming. One purpose of the forming operation is to compress the mix into a dense mass so that pitch-coated filler particles and flour are in intimate contact. For most applications, a primary goal in the production of graphite is to maximize density; this goal begins by minimizing void volume in the formed, green, product. Another purpose of the forming step is to produce a shape and size as near that of the finished product as possible. This reduces raw material usage and cost of processing graphite that cannot be sold to the customer and must be removed by machining prior to shipment. Two important methods of forming are extrusion and molding.

Extrusion. This process is used to form most carbon and graphite products. In essence, extrusion presses comprise a removable die attached by means of an adapter to a hollow cylinder called a mud chamber. The cylinder is charged with mix that is extruded in a number of ways depending on the press design. For one type of press, the cooled mix is introduced into the mud chamber in the form of plugs that are molded in a separate operation. A second type of extruder called a tilting press makes use of a moveable mud chamber-die assembly to eliminate the need for precompacting the cooled mix. Loading occurs directly from coolers with the assembly in the vertical position; the mixture is extruded with the assembly in the horizontal position. A third type of extrusion press makes use of an auger to force mix through the die. This press is used principally with fine-grained mixes because of its tendency to break down large particles.

The basic steps in the extrusion operation when a tilting press is used are depicted in Figure 2. The cooled mix is usually fed to the press on a conveyor belt where it is discharged into the mud chamber in the vertical position. A ram descends on the filled chamber, tamping the mix to compact the charge. A closing plate located in the pit beneath the press is often used to seal off the die opening, thereby preventing the mix from extruding during the application of high tamping pressures. In addition, a vacuum can be applied to the mud chamber during tamping to remove entrapped air. The filling and tamping procedures are repeated until the mud chamber is filled with tamped mix and then rotated back to the horizontal position. The extrusion ram then enters the mud cylinder forcing the mix through the die at 3–15 MPa (30–148 atm). A guillotinelike knife located near the die outlet cuts the extruded stock to the desired length. Round products are rolled into a tank of water where the outer portions are quickly cooled to prevent distortion of the plastic mass. Products having large rectangular cross-sections may be transferred from the press to the cooling tank by means of an overhead crane. Water temperatures are regulated to avoid cracking as a result of too rapid cooling. Products with smaller cross-sections, such as 32 × 152 × 810 mm plates used as anodes, may be cooled in air on steel tables. Bulk densities of green products range typically from 1.75–1.80 g cm^3.

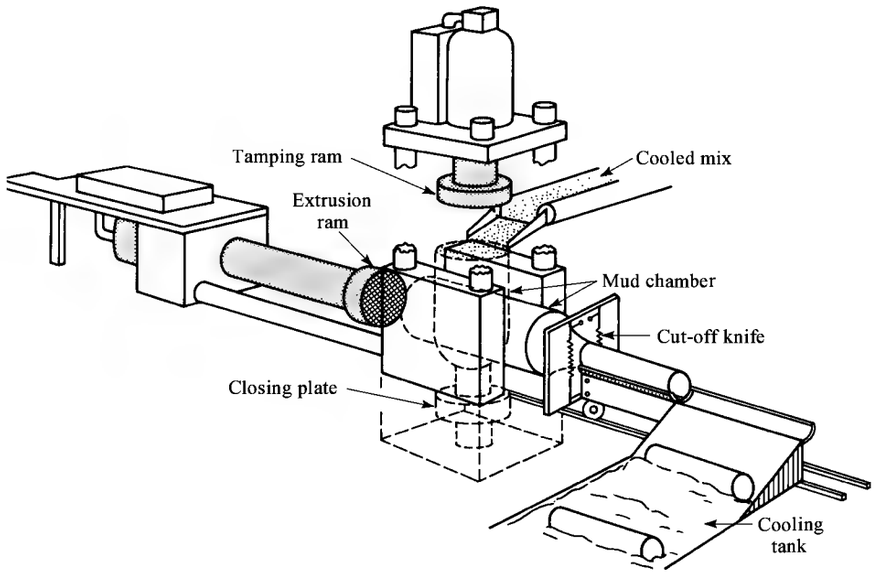

Fig. 2. Tilting extrusion press.

Courtesy of UCAR Carbon Technology Corp.

The anisotropy, usually observed in graphite products, is established in the forming operation. In extruded products, the anisotropic coke particles orient with their long dimensions parallel to the extrusion direction. The layer planes of the graphite crystals are predominantly parallel to the long dimension of the coke particle. Accordingly, the highly anisotropic properties of the single crystal are translated, to a greater or lesser degree depending on several factors, to the graphite product. The most important of these factors are coke type, particle size, and the ratio of die-to-mud chamber diameters. The more needlelike the coke particle, the greater the difference is between properties with-grain (parallel to the extrusion direction) and cross-grain. The use of smaller particles in the mix design also increases this property difference; the presence of large particles interferes with the alignment process. As the ratio of mud cylinder-to-die diameter increases, the with-grain to cross-grain ratios of strength and conductivity increase, whereas the with-grain to cross-grain ratios of resistivity and expansion coefficient decrease. Thus anisotropy is increased for the same coke type and mix design when going from a 600 mm diameter die to a 400 mm diameter die on the same extrusion press. As a result of particle orientation in extruded graphitized products, strength, Young's modulus, and thermal conductivity values are greater; whereas, electrical resistivity and coefficient of thermal expansion are smaller in the with-grain direction than in the two cross-grain directions.

Molding. Molding is the older of the two forming methods and is used to form products ranging in size from brushes for motors and generators to billets as large as 1.75 m diameter by 1.9 m in length for use in specialty applications.

Several press types are used in molding carbon products. The presses may be single-acting or double-acting, depending on whether one or both platens move to apply pressure to the mix through punched holes in either end of the mold. The use of single-acting presses is reserved for products whose thicknesses are small compared with their cross-sections. As thickness increases, the acting pressure on the mix diminishes with distance from the punch because of frictional losses along the mold wall. Acceptable thicknesses of molded products can be increased by using double-acting presses that apply pressures equally at the top and bottom of the product.

Jar molding is another method used to increase the length of the molded piece and keep nonuniformity within acceptable limits. By this technique, the heated mold is vibrated as the hot mix is introduced, thus compacting the mix during the charging operation. Pieces as large as 2.5 m in diameter and 1.8 m in length have been molded in this way; the green densities are comparable with those obtained in extruded materials.

Smaller products, such as brushes and seal rings, are often molded at room temperature from mix that is milled after cooling. When binder levels exceed approximately 30% of the mix, the compacted milled mix has sufficient green strength to facilitate handling in preparation for the baking operation.

In a typical hot molding operation to form a 1.7 m diameter billet 1.3 m long, approximately 7200 kg of mix at 160°C is introduced into a steam heated mold without cooling. The platens of the press compact the mix at ca 5 MPa (49 atm), holding this pressure for 15–30 min. The cooling step for pieces of this size is the most critical part of the forming operation. Owing to the low thermal conductivity of pitch, 0.13 W (m·K) (7), and its relatively high expansion coefficient at 25–200°C (4.5×10^{-4} °C) (8), stresses build rapidly as the outer portions of the piece solidify. If cooling is too rapid, internal cracks are formed that are not removed in subsequent processing steps. As a result, a cooling schedule is established for each product size and is carefully followed by circulating water of various temperatures through the mold for specified time periods. When the outside of the piece has cooled sufficiently, it is stripped from the mold and the cooling operation continued by direct water spray for several hours. If cooling is stopped too soon, heat from the center of the piece warms the pitch binder to a plastic state, resulting in slumping and distortion. The cooled piece is usually stored indoors prior to baking in order to avoid extreme temperature changes that may result in temperature gradients and damage to the structure. Bulk density of the green billet is usually 1.65–1.70 g/cm^3.

As with extruded products, molded pieces have a preferred grain orientation. The coke particles are aligned with their long dimensions normal to the molding direction. Thus the molded product has two with-grain directions and one cross-grain direction which coincides with the molding direction. Strength, modulus, and conductivity of molded graphites are higher in both with-grain directions and expansion coefficient is higher in the cross-grain direction. Isostatic molding is a forming technique used to orient the coke filler particles randomly; thereby imparting isotropic properties to the finished graphite. One approach to isostatic molding involves placing the mix or blend into a rubber container capable of withstanding relatively high molding temperatures. The container is evacuated then sealed and placed in an autoclave that is closed and filled with heated oil. The oil is then pressurized to compact the mass, which may then be processed in the usually way to obtain isotropic graphite. Cold isostatic molding is also used. In this process, room temperature water fills the autoclave and is pressurized to compact the mass.

Baking. In the next stage, the baking operation, the product is fired to 800–1000°C. One function of this step is to convert the thermoplastic pitch binder to solid coke. Another function of baking is to remove most of the shrinkage in the product associated with pyrolysis of the pitch binder at a slow heating rate. This procedure avoids cracking during subsequent graphitization where very fast firing rates are used. The conversion of pitch to coke is accompanied by marked physical and chemical changes in the binder phase, which if conducted too rapidly, can lead to serious quality deficiencies in the finished product. For this reason, baking is generally regarded as the most critical operation in the production of carbon and graphite.

Several studies discuss the kinetics of pitch pyrolysis and indicate, in detail weight loss and volatile evolution as functions of temperature (9,10). Weight losses of 30–40% occur, indicating that for every 500 kg of green product containing 20% pitch, 30–40 kg of gas must escape. In terms of gas volume, approximately 150 cm^3 of volatiles at standard conditions must be evolved per gram of pitch binder during the baking operation. The product in the green state is virtually impermeable, and the development of a venting porosity early in the bake must be gradual to avoid a grossly porous or cracked

structure. The generation of uniform structure during the bake is made more difficult by the poor thermal conductivity of pitch. Long firing times are usually needed to drive the heat into the center of the product, which is necessary for pitch pyrolysis and shrinkage. If the heating rates exceed a value which is critical for the size and composition of the product, differential shrinkage leads to splitting. Shrinkage during baking is of the order of 5% and increases with increasing pitch content. Added to these difficulties is the complete loss of mechanical strength experienced by the product in the 200–400°C range where the pitch binder is in a liquid state. To prevent slumping and distortion during this period, the stock must be packed in carefully sized coke or sand, which provides the necessary support and is sufficiently permeable to vent the pitch volatiles.

A variety of baking furnaces are in use to provide the flexibility needed to bake a wide range of product sizes and to generate the best possible temperature control. One common baking facility is the pit furnace, so named because it is positioned totally or partially below ground level to facilitate improved insulation. In essence, the pit furnace is a box with ceramic brick walls containing ports of flues through which hot gases are circulated. Traditionally, natural gas has been the fuel used to fire pit furnaces; however, pit furnaces can also be converted to use fuel oil (see FURNACES, FUEL FIRED).

Another common baking facility is the so-called ring furnace; one form of this is depicted in Figure 3. Two equal rows of pit furnaces are arranged in a rectangular ring. Ports in the furnace walls permit the heated gases from one furnace to pass to the next until the cooled gases are exhausted by a movable fan to a flue leading to a stack. A movable burner, in this case located above one furnace, fires it to a predetermined off-fire temperature. The firing time per furnace is 18–24 h. When the desired temperature has been reached, the burner is moved to the adjacent furnace which has been heated by gases from the most recently fired pit. At the same time, the fan is moved to a furnace that has just been packed. This process continues, with packing, unloading, and cooling stages separating the fan and the burner. Cycle times in this furnace are three to four weeks. Thermally, the ring furnace is highly efficient but it has the disadvantage that very little control can be exercised over heating rates.

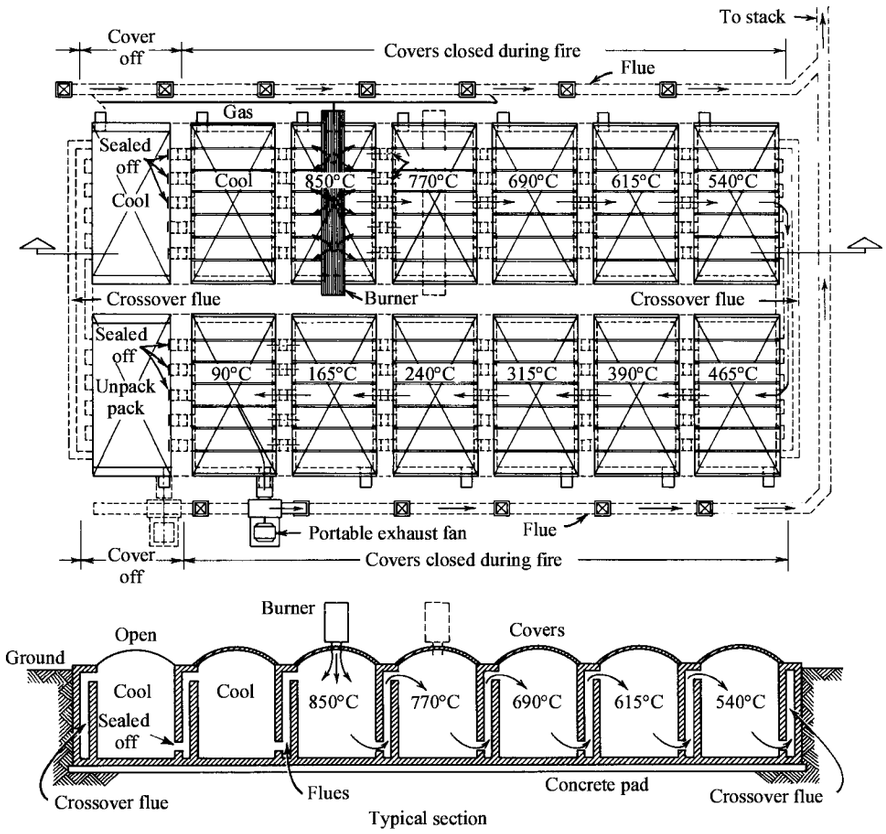

Fig. 3. Ring furnace system.

Courtesy of UCAR Carbon Technology Corp.

A more recent development is the carbottom furnace, which is an above ground rectangular kiln; the bottom is mounted on wheels and set on tracks so it is movable. The carbottom is isolated from the heating chamber by a water seal. These furnaces provide improved temperature and pressure control and better uniformity.

In addition, the development of stainless steel cans, saggers, into which green stock is loaded and then surrounded by packing media, has improved furnace heating effectiveness by reducing the ratio of packing media to green electrode. The can diameter is slightly larger than the stock diameter to accommodate this process. Beside reducing total energy requirements as much as 60–70%, the sagger allows the use of automated equipment in loading, unloading, and handling of the electrodes (11).

The firing schedules used in the baking operation vary with furnace type, product size, and binder content. A bulk furnace packed with 610 × 810 × 4600 mm pieces of specialty graphite may require six weeks to fire and an additional three to four weeks to cool. In contrast, very small products, such as seal rings, may be baked in tunnel kilns in a few hours. A sagger furnace containing electrodes may require 12–14 days to reach final temperature with an additional 3–5 days to cool. Firing rates early in the baking schedule are reduced to permit pitch volatiles to escape slowly, minimizing damage to the structure. For most carbon products, temperatures must be well below 400°C prior to unpacking to avoid cracking because of thermal shock. The product is scraped or sanded to remove adhering packing materials and is then weighed, measured, and inspected prior to being stored for subsequent processing. Some products that are sold in the baked state are machined at this stage. Baked products include submerged arc-furnace electrodes, cathode blocks for the electrolytic production of aluminum, and blast furnace lining blocks.

Impregnation. In some applications, the baked product is taken directly to the graphitizing facility for heat treatment to 3000°C. However, for many high performance applications of graphite, the properties of stock processed in this way are inadequate. The method used to improve those properties is impregnation with coal-tar or petroleum pitches. The function of the impregnation step is to deposit additional pitch coke in the open pores of the baked stock, thereby improving properties of the graphite product. Table 1 shows the graphite properties of unimpregnated and impregnated stock 150–300 mm diameter and containing 1.5 mm particles as the largest particle.

Table 1. Effect of One Pitch Impregnation on Graphite Properties

Property	Unimpregnated[a]		Impregnated[b]	
	wg[c]	ag[d]	wg[c]	ag[d]
Young's modulus, GPa[e]	7.4	4.4	11.0	6.3
flexural strength, MPa[f]	10.	7.1	17	13
tensile strength, MPa[f]	5	4.4	8.1	7.3
compressive strength, MPa[f]	21	21	34	33
permeability, μm^2[g]	0.39	0.35	0.19	0.16
coefficient of thermal thermal expansion, 10^{-6} °C	1.3	2.7	1.5	3.1
specific resistance, $\mu\Omega$·m	8.8	13.0	7.6	11.0

[a] Bulk density 1.6 g mL.

[b] Bulk density 1.7 g mL.

[c] With the grain, ie, samples cut parallel to the molding plane or extrusion axis.

[d] Across the grain, ie, samples cut perpendicular to the molding or extrusion force.

[e] To convert GPa to psi, multiply by 145,000.

[f] To convert MPa to psi, multiply by 145.

[g] To convert μm^2 to darcys, divide by 0.9869.

Further property improvements result from additional impregnation steps separated by rebaking operations. However, the gains realized diminish quickly, for the quantity of pitch picked up in each succeeding impregnation is approximately half of that in the preceding treatment. Many nuclear and aerospace graphites are multiple pitch-treated to achieve the greatest possible assurance of high performance.

During the baking operation, binder pitch exuding the product surface creates a dense impermeable skin. In addition, the exuding pitch causes packing material to adhere to the baked stock. The skin and the packing material must be removed by sanding, scraping, or machining before the stock can be impregnated on a reasonable time cycle. Unless this operation is properly performed, the impregnant may not reach the center of the product and a so-called dry core results. When this condition exists, the product usually splits during graphitization as a consequence of the greater concentration of pitch and greater shrinkage in the outer portions of the stock. The likelihood of a dry core increases with the quinoline-insoluble solids content of the impregnant. During the impregnation process, the insolubles form a filter cake of low permeability on the stock surface, reducing the penetrability of the impregnant. Quinoline insolubles significantly greater than 5% reduce the penetration rate and increase the incidence of dry cores.

A schematic diagram of the pitch impregnation process is shown in Figure 4. Before it is placed in an autoclave, the skinned baked stock is preheated to 250–300°C to thoroughly dry it and to facilitate free flow of the molten impregnant into the open pores. The first step in the impregnation process is to evacuate the stock to pressures below 3.5 kPa (26 mm Hg) for a period of one hour or more depending on the size and permeability of the stock. Unless the stock is adequately evacuated, the remaining air prevents thorough penetration of the impregnant to the center of the product. Heated pitch is then introduced by gravity flow into the autoclave from a holding tank until the charge is completely immersed. The system is then subjected to pressures of 700–1500 kPa (~7–15 atm) for several hours to shorten the time for pitch penetration. When the pressure cycle has been completed, the pitch is blown back to the holding tank by means of compressed air. The autoclave is then opened, and the stock is transferred to a cooler where water and or circulating air accelerate the cooling process. After cooling, the stock is weighed to determine the quantity of pitch picked up. If the pickup is below a specified limit, the stock is scrapped. Depending on the density of the baked stock, the pickup is 12–16% on the first impregnation and 6–8% on the second impregnation.

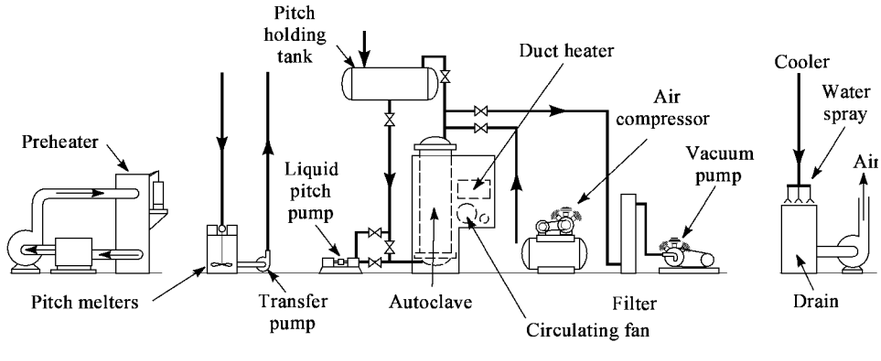

Fig. 4. Pitch impregnation system. Courtesy of UCAR Carbon Technology Corp.

If the stock is to receive a second impregnation, it must be rebaked. In the past, stock containing raw impregnating pitch could be graphitized directly. However, the air polluting effect caused by this practice has made rebaking a necessary preliminary step to graphitization in order to achieve effective environmental control.

Graphitization. Graphitization is an electrical heat treatment of the product to ca 3000°C. The purpose of this step is to cause the carbon atoms in the petroleum coke filler and pitch coke binder to orient into the graphite lattice configuration. This ordering process produces graphite with intermetallic properties that make it useful in many applications.

Very early in the carbonization of coker feeds and pitch, the carbon atoms are present in distorted layers of condensed benzene ring systems formed by the polymerization of the aromatic hydrocarbons in these materials. X-ray studies of raw coke, for example, show two-dimensional order at that early stage of graphite development (12). As the temperature of coke increases, the stack height of the layer plane increases. The layers are skewed about an axis normal to them, however, and it is not until a temperature of ca 2200°C is reached that three-dimensional order is developed. As the graphitizing temperature is increased to 3000°C, the turbostratic arrangement of the layer planes is effectively eliminated, and the arrangement of the carbon atoms approaches that of the perfect graphite crystal. Depending on the size and orientation of these crystals, the properties of manufactured graphites can be varied controllably to suit a number of critical applications.

The furnace that made the graphite industry possible was invented in 1895 by Acheson (13) and is still in use today with only minor modifications. It is an electrically fired furnace capable of heating tons of charge to temperatures approaching 3000°C. The basic elements of the Acheson furnace are shown in Figure 5. The furnace bed is made up of refractory tiles supported by concrete piers. The furnace ends are U-shaped concrete heads through which several graphite electrodes project into the pack. These electrodes, which are water-cooled during operation, are connected by copper bus work to the secondary of a transformer. The product is placed on a layer of metallurgical coke with its long axis transverse to current flow. Although a cylindrical product is shown in Figure 5, any product shape can be graphitized in the Acheson furnace so long as the product pieces are carefully spaced. This feature of the Acheson furnace makes it extremely versatile. The spacing between pieces may vary from less than a centimeter to several centimeters, depending on

the shape and size of the product. With the product in place, a coarsely sized metallurgical coke, called resistor pack, is used to fill the interstices between pieces; most of the heat needed to reach graphitizing temperatures is generated in the resistor material. Once the charge and resistor material are loaded, the furnace is covered with a finer blend of metallurgical coke, sand, and silicon carbide to provide thermal and electrical insulation. Concrete side blocks, usually 0.5–1 m from the charge ends, are used to retain the insulation. The procedure for loading a furnace usually requires one day.

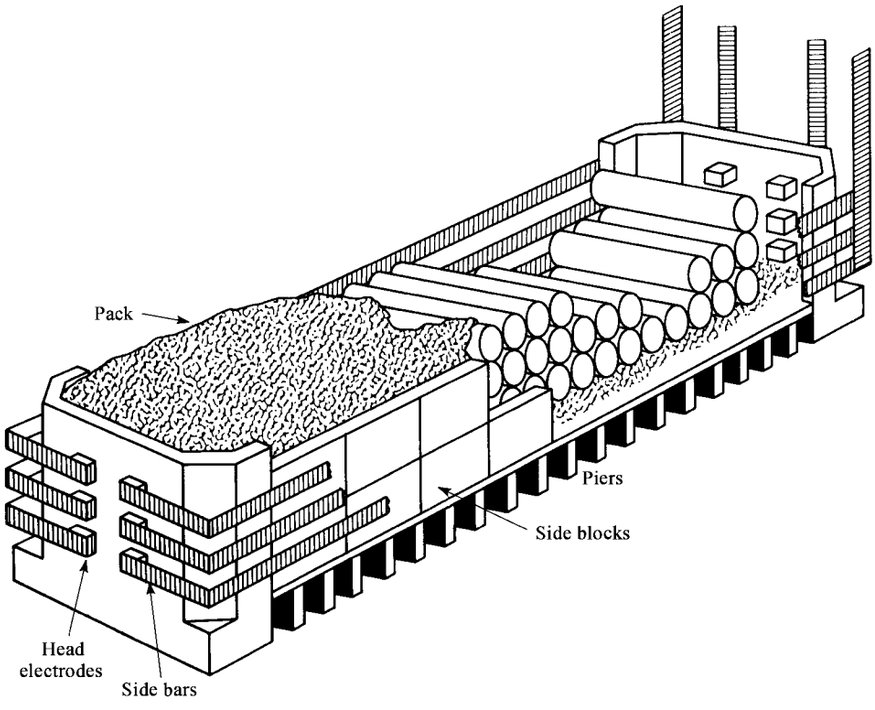

Fig. 5. The Acheson furnace. Courtesy of UCAR Carbon Technology Corp.

Acheson furnace sizes may vary, depending on the product size and the production rate desired. Typically, the furnace may be 12–15 m by 3–3.5 m. Loads ranging from 35–55 metric tons of product are charged to these furnaces. The transformers used are rated 4000–6000 kW and are capable of delivering up to 60,000 A to the charge. Heating rates are usually 40–60°C h; the total firing time is approximately three days. At the end of this time, the product temperatures are 2800–3000°C. Total power input varies, depending on the product and load size; for graphite electrodes, total power (energy) inputs average 4.5 kWh kg, and total power inputs in excess of 9 kWh kg may be used in the thermal purification of nuclear graphites. Following the heating cycle, 8–10 days are needed to cool and unload the furnace. The total cycle time on an Acheson furnace is ca two weeks. The cooling procedure is hastened by the gradual removal of pack with care to leave sufficient cover to prevent oxidation of the product. The insulation and resistor materials are screened to specified sizes and proportions for reuse; new materials are added as necessary. The product is cleaned and inspected prior to being measured and weighed for bulk density and resistivity determinations. If the properties are within specified limits, the product is stored and is ready for machining.

Furnaces other than the Acheson furnace are used commercially but on a much smaller scale and usually for smaller products. For example, electrographitic brushes are graphitized in tube furnaces, wherein a current-carrying graphite tube is the heating element. These furnaces are particularly useful in the laboratory because of the ease with which they can be loaded and unloaded without the need for handling large quantities of packing material. Inductively-heated furnaces are also used commercially to graphitize a limited number of products, such as some aerospace grades and carbon fibers. These furnaces, also popular in the laboratory, consist basically of a cylindrical graphite shell susceptor positioned inside a water-cooled copper coil. High frequency power supplied to the coil induces current to flow in the susceptor, heating it and causing it to radiate heat to the contained charge (see FURNACES, ELECTRIC).

Several patents (14–18) have been issued describing a process for graphitization where the carbon charge to be heated is placed in a longitudinal array and covered with insulation to prevent heat losses and oxidation of the charge. An electric current is passed directly through the carbon array, generating within the carbon the heat required to raise the carbon to the graphitization temperatures. These furnaces, because of the direct heating of the carbon charge, utilize less than 4.4 kWh kg and can be cycled from load-to-reload in less than a week (11).

Puffing. In the temperature range of 1500–2000°C, most petroleum cokes and coal-tar pitch cokes undergo an irreversible volume increase known as puffing. This effect in petroleum cokes has been associated with thermal removal of sulfur and increases with increasing sulfur content. Some mechanisms other than sulfur removal may be more dominant in coal-tar pitch cokes. Because of the recent emphasis on the use of low sulfur fuels, many of the sweet crudes that had been used to produce coker feedstocks are now being processed as fuels. Desulfurization of sour crudes or coker feeds is possible but expensive. The result is an upward trend in the sulfur content of many petroleum cokes, leading to greater criticality in heating rate in the puffing temperature range during graphitization.

Many studies of the puffing phenomenon and of means for reducing or eliminating it have been made (19–22). As a general rule, puffing increases as particle size increases and is greater across the product grain. Depending on particle size and on the product size, heating rates must be adjusted in the puffing range to avoid splitting the product. Fortunately, the use of puffing inhibitors has eased the problem and has permitted the use of graphitization rates greater than would otherwise be possible.

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PROPERTIES OF MANUFACTURED GRAPHITE

Physical Properties

The graphite crystal, the fundamental building block for manufactured graphite, is one of the most anisotropic bodies known. Properties of graphite crystals illustrating this anisotropy are shown in Table 1 (1). Anisotropy is the direct result of the layered structure with extremely strong carbon–carbon bonds in the basal plane and weak bonds between planes. The anisotropy of the single crystal is carried over in the properties of commercial graphite, though not nearly to the same degree. By the selection of raw materials and processing conditions, graphites can be manufactured with a very wide range of properties and degree of anisotropy. The range of room temperature properties, attainable for various forms of graphite, is shown in Figures 1 and 2 (1). The range extremities represent special graphites having limited industrial utility, whereas the bulk of all manufactured graphites fall in the bracketed areas marked conventional.

Table 1. Properties of Graphite Crystals at Room Temperature[a]

Property	Value in basal plane	Value across basal plane
resistivity, $\mu\Omega\cdot m$	0.40	ca 60
elastic modulus, GPa[b]	1020	36.5
tensile strength (est), GPa[b]	96	34
thermal conductivity, W (m·K)	ca 2000	10
thermal expansion, $°C^{-1}$	0.5×10^{-6}	27×10^{-6}

[a] Ref. 1.

[b] To convert GPa to psi, multiply by 145,000.

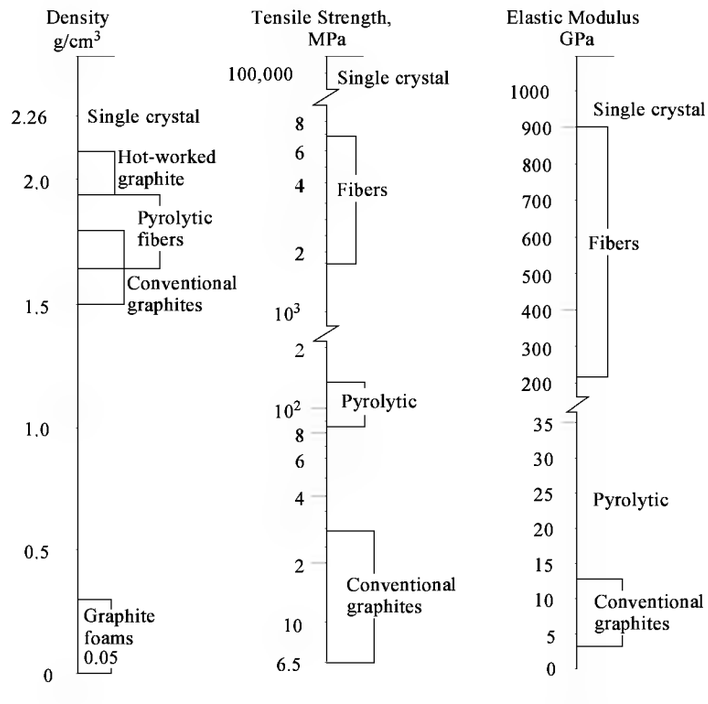

Fig. 1. With-grain mechanical properties of artificial graphite (1). To convert MPa to psi, multiply by 145.

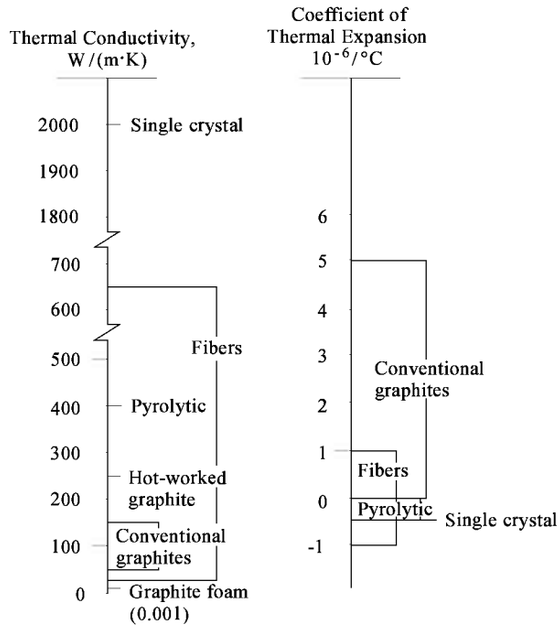

Fig. 2. With-grain thermal properties of artificial graphite (1).

The directional properties of manufactured graphite arise in the following way. When the coke aggregate is crushed and sized, the resulting coke particles tend to have one axis longer than the other two. As the plastic mix of particles and binder pitch is formed into the desired shape, the long axis of particles tends to align perpendicularly to the molding force in molded graphite and parallel to the extrusion force in extruded graphites. The particle alignment is preserved during the subsequent processing so that properties of the finished graphite have an axis of symmetry that is parallel to the forming force. Properties in the plane perpendicular to the axis of symmetry are essentially independent of direction. Samples cut parallel to the molding force for molded graphites or perpendicular to the extrusion force for extruded graphites are designated as cross-grain. Samples cut parallel to the molding plane of molded graphites or parallel to the extrusion axis for extruded graphites are designated as with-grain. A number of special test procedures for determining the properties of carbon and graphite have been adopted by ASTM (2).

Manufactured graphite is a composite of coke aggregate (filler particles), binder carbon, and pores. Most graphites have a porosity of 20–30%, though special graphites can be made that have porosity well outside this range. Manufactured graphite is a highly refractory material that has been thermally stabilized to as high as 3400°C. At temperatures in excess of 3500°C, the vapor pressures of the various carbon species in the manufactured graphite begin to exceed 10 kPa (~0.1 atm) and vapor transport occurs. The strength of graphite increases with temperature to 2200°C; above 2200°C, graphite becomes plastic and exhibits viscoelastic creep under load (3). Graphite has high resistance to thermal shock, a property that makes it a more valuable structural material at higher temperatures than most metals and alloys. For many applications of graphite, one or more of the following characteristics are important: density, elastic modulus, mechanical strength, electrical and thermal conductivity, and thermal expansion.

Electrical Properties.

Manufactured graphite is semimetallic in character with the valence and conduction bands overlapping slightly (4–6). Conduction is by means of an approximately equal number of electrons and holes that move along the basal planes. The resistivity of single crystals as measured in the basal plane is approximately 0.40 $\mu\Omega$·m; this is several orders of magnitude lower than the resistivity across the layer planes (7–9). Thus the electrical conductivity of formed graphite is dominated by the conductivity in the basal plane of the crystallites and is dependent on size, degree of perfection, orientation of crystallites, and on the effective carbon–carbon linkages between crystallites. Manufactured graphite is strongly diamagnetic and exhibits a Hall effect, a Seebeck coefficient, and magnetoresistance. The green carbon body is practically nonconductive; however, heat treatment at 800°C decreases the resistivity by several orders of magnitude, and thereafter resistivity decreases slowly. After graphitization to over 2500°C, the room temperature electrical resistivity may range from a few hundred to a few tenths $\mu\Omega$·m, depending on the type of raw materials used. Graphites made from petroleum coke usually have a room temperature resistivity range of 5–15 $\mu\Omega$·m and a negative temperature coefficient of resistance to about 500°C, above which it is positive. Graphites made from a carbon black base have a resistivity several times higher than those made from petroleum coke, and the temperature coefficient of resistance for the former remains negative to at least 1600°C.

Thermal Conductivity.

Compared with other refractories, graphite has an unusually high thermal conductivity near room temperature (10); above room temperature, the conductivity decreases exponentially to approximately 1500°C and more slowly to 3000°C (11). With the grain, the thermal conductivity of manufactured graphite is comparable with that of aluminum; against the grain, it is comparable to that of brass. However, graphite is similar to a dielectric solid in that the principal mechanism for heat transfer is lattice vibrations. The electronic component of thermal conductivity is less than 1%. Graphite does not obey the Wiedemann-Franz Law; however, at room temperature the ratio of thermal and electrical conductivities is equal to approximately 0.126 when the thermal conductivity is in W/(m·K) and the electrical conductivity is in S/(m·Ω) (12,13). For most graphites, a value of thermal conductivity at room temperature accurate to ±5% can be obtained from the measured value of the electrical conductivity.

Coefficient of Thermal Expansion (CTE). The volumetric thermal expansion (VTE) of manufactured graphite expressed in equation 1 is anomalously low when compared to that of the graphite single crystal, where wg designates with-grain and cg, cross-grain.

$$VTE = CTE_{wg} + 2\,CTE_{cg} \tag{1}$$

At room temperature, the volume coefficient of thermal expansion of a single crystal is approximately 25×10^{-6} °C (14,15), whereas those of many manufactured graphites fall in the range of $4-8 \times 10^{-6}$ °C. There are exceptions and some commercially available, very fine-grain, near-isotropic graphites have a volumetric expansion as high as two-thirds the value for the single crystal. The low value of volume expansion of most manufactured graphite has been related to the microporosity within the coke particles. The microcracks within the coke particle accommodate the large *c*-axis expansion of graphite crystallites (16–18) and effectively neutralize it. The coefficient of thermal expansion is somewhat sensitive to the filler particle sizing and to the method of processing, but the anisotropy and perfection degree of filler carbon particles largely determine the expansion characteristics of the finished graphite. Except for differences in absolute values, plots of the CTEs of manufactured graphite versus temperature are essentially parallel to each other, showing that

the change in CTE with temperature is approximately the same for all graphites at high temperatures. The mean linear coefficient of thermal expansion between room temperature and any final temperature can be obtained by adding the value of CTE for the temperature interval 20–100°C to the appropriate factor which varies from 0 at 100°C to 2.52×10^{-6} at 2500°C (19). This method is valid for stock of any grain orientation.

Mechanical Properties. The hexagonal symmetry of a graphite crystal causes the elastic properties to be transversely isotropic in the layer plane; only five independent constants are necessary to define the complete set. The self-consistent set of elastic constants given in Table 2 has been measured in air at room temperature for highly ordered pyrolytic graphite (20). With the exception of c_{44} these values are expected to be representative of those for the graphite single crystal. Low values of shear and cleavage strengths between the layer planes compared with very high C–C bond strength in the layer planes suggest that graphite always fails through a shear or cleavage mechanism. However, the strength of manufactured graphite depends on the effective network of C–C bonds across any stressed plane in the graphite body. Until these very strong bonds are broken, failure by shear or cleavage cannot take place. Porosity affects the strength of graphite by reducing the internal area over which stress is distributed and by creating local regions of high stress. Because of the complexity of the graphite structure, a simple analytical model of failure has not been derived (21). The stress–strain relation for bulk graphite is concave toward the strain axis. The relaxation of the stress leads to a small residual strain; repeated stressing to larger loads followed by gradual relaxation leads to a set of hysteresis loops contained within the stress–strain envelope (3,22–26). Each successive load causes an increase in the residual strain and results in a decreased modulus for the sample. The residual strain can be removed by annealing the sample to the graphitizing temperature after which its original stress–strain response is restored. In the limit of zero stress, the elastic modulus of graphite is the same in compression and tension, and is equal to the modulus derived from dynamic measurements (27). The modulus of graphite is weakly dependent on temperature, increasing with temperature to approximately 2000°C and decreasing thereafter. The strain at rupture of most graphites is 0.1–0.2%; however, values of strain at rupture approaching 1.0% have been obtained for specially processed, fine-grain graphites (28). Graphite exhibits measurable creep under load and at temperatures above 1600°C, but for most applications creep can be neglected below 2200°C. As the temperature is increased above 2500°C, the creep rate increases rapidly and the short-time strength decreases rapidly.

Table 2. Elastic Constants of Graphite[a]

c_{11}	1.06 ± 0.002	s_{11}	0.98 ± 0.03
c_{12}	0.18 ± 0.02	s_{12}	0.16 ± 0.06
c_{13}	0.015 ± 0.005	s_{13}	0.33 ± 0.08
c_{33}	0.0365 ± 0.0010	s_{33}	27.5 ± 1.0
c_{44}	0.00018 0.00035	s_{66}	2.3 ± 0.2

[a] Units c_{ij} (stiffness constant) in TPa, s_{ij} (compliance constant) in $(GPa)^{-1}$. To convert TPa to psi, multiply by 145,000,000.

Thermal shock resistance is a primary attribute of graphite and a number of tests have been devised in attempts to establish a quantitative method of measurement (29,30). These tests, which establish very large thermal gradients in small specially shaped samples, continue to give only qualitative data and permit establishment of only the relative order of shock resistance of different graphites. A commonly used thermal shock index is the ratio of the thermal conductivity and strength product to the expansion coefficient and modulus product (31). At high temperatures values of this index for graphite are higher than for any other refractory material. To show the range of property values of graphite, several properties for a very coarse-grain graphite and a very fine-grain graphite are given in Table 3 (27,32).

Table 3. Properties of Fine- and Coarse-Grain Graphites[a]

	Thermal conductivity, W/(m·K)		CTE[b], cm/(cm·10^6 °C)			Tensile[d]				Compression[d]			
						Modulus, GPa		Strength, MPa		Modulus, GPa		Strength, MPa	
Temp., °C	wg	ag	wg	ag	Specific heat[c], kJ/(kg·K)	wg	ag	wg	ag	wg	ag	wg	ag
					Fine-grained graphite, 180 μm maximum grain size								
21	150	114	2.15	3.10	0.63	11.5	7.9	17.4	15.0	9.7	7.2	26.6	20.1
260	117	93	2.50	3.46	1.30	11.6	8.0	19.3	17.2	10.0	7.4	27.9	21.7
538	91	72	2.82	3.84	1.63	11.7	8.1	21.7	19.7	10.3	7.6	29.3	23.4
816	73	57	3.16	4.12	1.80	11.9	8.3	24.1	22.1	10.6	7.9	30.9	25.2
1093	60	46	3.45	4.45	1.95	12.1	8.6	26.0	24.3	11.4	8.3	32.4	26.9
1371	52	40	3.70	4.69	2.03	12.5	9.0	28.3	26.2	12.4	9.0	35.2	29.3
1649	46	35	3.95	4.91	2.11	13.2	9.6	29.9	27.9	13.4	9.7	38.1	31.6
1927	42	32	4.17	5.16	2.16	13.7	10.5	31.0	29.3	13.4	9.7	32.2	37.2
2204	40	29	4.35	5.39	2.18	11.5	8.4	31.7	30.1	12.1	9.0	37.9	32.6
2482	38	28	4.58	5.71	2.20	8.0	5.9	31.0	29.3	10.0	7.9	32.4	26.6
2760	36	28	4.83	6.04	2.20	5.2	4.3	26.9	24.8	7.9	6.2	26.6	19.1
					Coarse-grained graphite, 6400 μm maximum grain size								
21	156	108	0.46	1.03		4.2	2.6	3.75	2.91	3.0	2.6	9.3	12.1
1371	30	22	2.4	3.2		5.8	2.9	5.34	4.54	3.4	2.8	12.0	14.7
1927	24	19	2.7	2.85		6.5	3.7	5.39	4.36	4.3	3.3	14.1	17.4
2427	24	20	3.0	4.2		5.6	3.0	7.32	5.17				

[a] wg with-grain; ag across-grain.

[b] CTE coefficient of thermal expansion.

[c] To convert kJ to kcal, divide by 4.184.

[d] To convert MPa to psi, multiply by 145.

Chemical Properties. The impurity (ash) content of all manufactured graphite is low, since most of the impurities originally present in raw materials are volatilized and diffuse from the graphite during graphitization. Ash contents vary from 1.5% for large diameter graphites to less than 10 ppm for purified graphites. Iron, vanadium, calcium, silicon, and sulfur are principal impurities in graphite; traces of other elements are also present (33). Through selection of raw materials and processing conditions, the producer can control the impurity content of graphites to be used in critical applications. Because of its porosity and relatively large internal surface area, graphite contains chemically and physically adsorbed gases. Desorption takes place over a wide temperature range, but most of the gas can be removed by heating in a vacuum at approximately 2000°C.

Graphite reacts with oxygen to form CO_2 and CO, with metals to form carbides, with oxides to form metals and CO, and with many substances to form laminar compounds (34,35). Of these reactions, oxidation is the most important to the general use of graphite at high temperatures. Oxidation of graphite depends on the nature of the carbon, the degree of graphitization, particle size, porosity, and impurities present (36). These conditions may vary widely among graphite grades. Graphite is less reactive at low temperatures than many metals; however, since the oxide is volatile, no protective oxide film is formed. The rate of oxidation is low enough to permit the effective use of graphite in oxidizing atmospheres at very high temperatures when a modest consumption can be tolerated. A formed graphite body alone will not support combustion. The differences in oxidation behavior of various types of graphite are greatest at the lowest temperatures, tending to disappear as the temperature increases. If an oxidation threshold is defined as the temperature at which graphite oxidizes at 1% per day, the threshold for pure graphite lies in the range of 520–560°C. Small amounts of catalyst, such as sodium, potassium, vanadium, or copper, reduce this threshold temperature for graphite by as much as 100°C but greatly increase the oxidation rate in the range of 400–800°C (33). Above 1200°C, the number of oxygen collisions with the graphite surface controls the oxidation reaction. Oxidation of graphite is also produced by steam and carbon dioxide; general purpose graphite has a temperature oxidation threshold of approximately 700°C in steam and 900°C in carbon dioxide. At very low concentrations of water and CO_2 there is also a catalytic effect of impurities on the oxidation behavior of graphite (37).

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APPLICATIONS OF BAKED AND GRAPHITIZED CARBON

Aerospace and Nuclear Reactor Applications

Graphite with its exceptional strength and thermal stability at high temperatures is a prime candidate material for many aerospace and nuclear applications. Its properties, through process modifications, are tailorable to meet an array of design criteria for survival under extremely harsh environmental operations.

Graphite is a lightweight structural material that retains most of its mechanical strength even at temperatures in excess of 2200°C. It has a high resistance to thermal shock and exhibits good neutron interaction characteristics and stability under irradiation. The ease of machining and commercial availability of graphite are other desirable qualities for these applications; however, oxidation at high temperatures presents a problem requiring oxygen protective systems for any prolonged use.

Aerospace and nuclear reactor applications of graphite demand high reliability and reproducibility of properties, physical integrity of product, and product uniformity. The manufacturing processes require significant additional quality assurance steps that result in high cost.

Aerospace. Graphite applications in the aerospace industry include rocket nozzle components, nose cones, motor cases, leading edges, control vanes, blast tubes, exit cones, thermal insulation, and any other applications where a rapid temperature rise and unusually high operating temperatures are encountered. Graphite is one of the few materials that can reasonably meet the demands encountered under these conditions. Of particular importance in this type of application are the excellent thermal properties of graphite, eg, high thermal shock resistance, high thermal stress resistance, and a strength increase with temperature increase. In addition, its excellent machinability makes it possible to maintain the required close tolerances for the machining of precision components for aerospace vehicles.

The erosion of graphite in nozzle applications is a result of both chemical and mechanical factors. Changes in temperature, pressure, or fuel-oxidizing ratio markedly affect erosion rates. Graphite properties affecting its resistance to erosion include density, porosity, and pore size distribution (see ABLATIVE MATERIALS).

The entrance cap, throat, and exit cone sections in a typical nozzle are frequently made or lined with conventional bulk graphite, especially in small nozzles where dimensional stability is extremely important, since a small change in dimension causes a relatively large change in performance. In other designs the throat may be made of conventional graphite with entrance cap and exit cone molded of carbon or graphite fibrous materials that serve as reinforcement for high temperature plastic materials. In larger nozzles, all three sections might be made of fiber-reinforced material because of high strength, light weight, and ease of construction of the composite materials.

Nose cones and leading edge components fabricated of graphite are used on both ballistic and glider-type reentry vehicles. Ballistic vehicles are exposed to short duration, extremely severe friction heating and oxidizing conditions upon reentry to the atmosphere. Glider-type reentry vehicles are exposed to less severe conditions for longer periods. Design technology and the ability to control properties of manufactured graphite favorably has increased its use in aerospace applications.

The severe operational environment of advanced high performance missiles and space vehicles imposes exacting requirements on structural components that must withstand temperatures of approximately 2000°C in oxidizing atmospheres. Extensive studies on coatings for the protection of graphite under these conditions has been carried out under U.S. Air Force funding (1). A thin coating of iridium metal (2) was found to be the only material that was totally satisfactory for the protection of graphite from oxidation at 2000°C.

Nuclear Applications. The strength of graphite at high temperatures and its behavior with respect to products of nuclear fission fusion make it a suitable material for nuclear moderators and reflectors, materials of construction, and thermal columns in various reactors. Since its use in the first nuclear reactor, CP-1, constructed in 1942 at Stagg Field, University of Chicago, many thousands of metric tons of graphite have been used for this purpose. Uranium–graphite moderators were used in the Calder Hall reactors for power generation. The advanced gas-cooled reactors (AGR), the high temperature gas-cooled reactors (HTGR), the molten salt breeder reactors (MSBR), and liquid metal fueled reactors (LMFR) all use graphite moderators. The thermal stability, resistance to corrosion, and high thermal conductivity of graphite make it a most suitable moderator material for consideration in advanced design, high temperature, atomic energy efficient nuclear reactors.

Graphite is chosen for use in nuclear reactors because it is the most readily available material with good moderating properties and a low neutron capture cross section. Other features that make its use widespread are its low cost, stability at elevated temperatures in atmospheres free of oxygen and water vapor, good heat transfer characteristics, good mechanical and structural properties, and excellent machinability.

Neutron economy in graphite occurs because pure graphite has a neutron capture cross section of only $0.0032 \pm 0.002 \times 10^{-24}$ cm^2. Taking into account the density of reactor grade graphite (bulk density 1.71 g cm^3), the bulk neutron absorption coefficient is 0.0003 cm. Thus a slow neutron may travel >32 m in graphite without capture.

The purity of reactor-grade graphite is controlled by raw material selection and subsequent processing and purification. High temperature purification is used for most applications; however, some moderator graphites applications require considerably higher purity levels such as halogen purification to remove extremely stable carbides, especially that of boron. The actual purity requirements are determined by the reactor design.

On exposure to high temperature radiation (3) over a long period of time, graphite undergoes dimensional changes. For example, graphite initially contracts on exposure to fast neutron doses, but the rate of contraction decreases with exposure until it reaches a minimum volume; further exposure causes volume expansion, with the rate of expansion increasing rapidly at neutron doses above 3×10^{22} neutrons cm^2 (>50 keV) in all bulk graphite tested to date. This behavior is caused by atomic displacements that take place when graphite is exposed to fast neutrons, resulting in anisotropic crystallite growth rates. The crystal expands in the c-axis direction and contracts in the α-axis directions. The bulk dimensional change depends on the geometrical summation of the individual crystallite changes and, hence, is dependent on the starting materials and the method of fabrication. The extent of radiation damage is also strongly dependent on the temperature of the graphite during irradiation. The severity of graphite radiation damage at high temperatures was underestimated since the magnitude of this temperature dependence was not recognized until about 1965.

Figure 1 shows the volume change in a conventional nuclear graphite during irradiations at various temperatures of relatively high fluxes. Figure 2 shows the length change in an isotropic nuclear graphite during irradiations at various temperatures at relatively high fluxes. The actual changes in dimensions are, of course, different from grade to grade and depend largely on the degree of anisotropy present in the graphite (3).

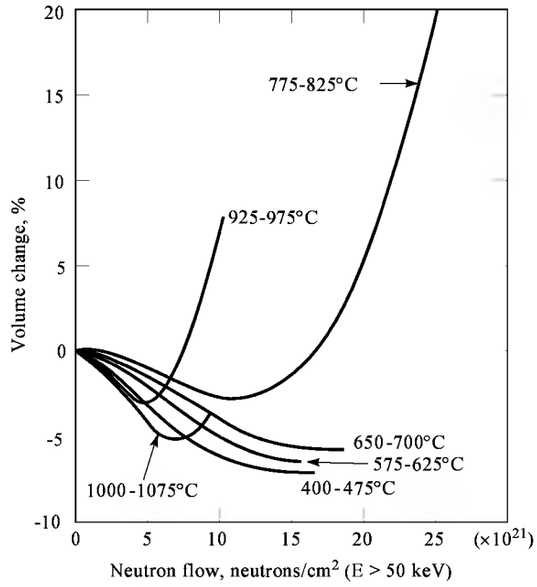

Fig. 1. Volume change in anisotropic graphite during General Electric Test Reactor (GETR) irradiations. Courtesy of Oak Ridge National Laboratory, managed by Martin Marietta Energy Systems, Inc. for the U.S. Department of Energy under Contract No. DE-AC05-840R21400.

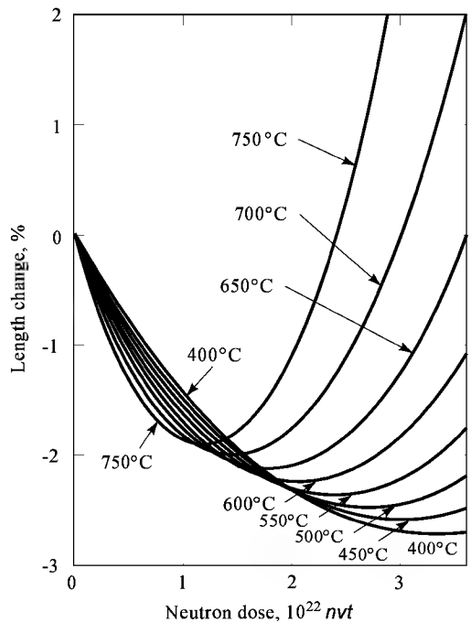

Fig. 2. Radiation-induced dimensional changes in isotropic graphite at various temperatures. nvt neutron(density)velocity·time.

Courtesy of Oak Ridge National Laboratory, managed by Martin Marietta Energy Systems, Inc. For the U.S. Department of Energy under Contract No. DE-AC05-840R21400.

Table 1 (4,5) lists some useful properties of several graphites used for moderators or reflectors in nuclear reactors. Reactor designers have taken advantage of graphite's properties in applying the material to other than moderator and reflector components, usually in conjunction with some other material.

Table 1. Properties of Nuclear Graphites

Property	Anisotropic graphite[a]	Isotropic graphite[b]
density, g cm^{3}	1.71	1.86
resistance, $\mu\Omega$·cm	735	1000
tensile strength, kPa[c]	9,930	46,172
coefficient of thermal expansion (CTE), 10^{6} °C		
with-grain	2.2	5.3
against-grain	3.8	5.3
anisotropy ratio (CTE ratio)	1.73	1.0
total ash, ppm	740	400
boron content, ppm	0.4	0.3

[a] Ref. 4.

[b] Ref. 5.

[c] To convert kPa to psi, multiply by 0.145.

Combined as an admixture with some forms of boron or other high neutron absorbing elements, graphite offers advantages as a neutron shield, control rod, or secondary shutdown material of high temperature stability, without danger of meltdown. In fast reactors, where high energy neutrons reach the shield region, the presence of carbon atoms slows these neutrons down to energies where the probability of capture in the neutron absorber greatly increases. Graphite also serves as a stable matrix for the neutron absorber because it is able to withstand neutron and localized alpha recoil damage, offering protection against gross shield degradation.

Bulk graphites are also used in the HTGR concept to support and surround the active fuel core. These components tend to be large, complex-shaped blocks and have been produced from commercial grades of molded or extruded graphites.

In combination with compounds of uranium or thorium, graphite offers advantages as a matrix for fissile or fertile reactor fuel in thermal reactors. In this instance, the graphite serves a dual purpose, as a moderator and as a stable disbursing phase for fuel. Its stability under irradiation and at high temperature aids in minimizing fuel degradation and permits longer useful fuel life. Because of its excellent thermal properties and mechanical integrity, graphite offers an excellent heat-transfer medium for heat removal and also resists thermal shock.

Chemical Applications

Carbon and graphite exhibit excellent resistance to the corrosive actions of acids, alkalies, and organic and inorganic compounds, an attribute that has fostered the use of graphite in process equipment where corrosion is a problem. Other than in the chemical process industries, graphite is used extensively in the steel, food, petroleum, pharmaceutical, and metal finishing industries. The high thermal conductivity and thermal stability of graphite have made it a useful material in heat exchangers and high temperature gas-spray coolers.

Manufactured carbon and graphite exhibit varying degrees of porosity depending on its method of preparation. Equipment fabricated from these materials must be operated essentially at atmospheric pressure; otherwise, some degree of leakage must be tolerated. Carbon used as a liner for tanks and vessels for the handling of highly corrosive inorganic acids such as hydrofluoric, nitric, phosphoric, sulfuric, and hydrochloric (6) is backed up by an impervious membrane of lead (7) or plastic to prevent seepage through the lining. The carbon lining protects the impermeable membrane material from adverse temperature and abrasion effects. Carbon linings have provided indefinite life with a minimum of maintenance.

Self-Supporting Structures. Self-supporting structures of carbon and graphite are used in a variety of ways. Water-cooled graphite towers serve as chambers for the burning of phosphorus in air. The high thermal conductivity of graphite allows rapid heat transfer to a water film on the outside of the tower, thereby maintaining inside wall temperature below 500°C, the oxidation temperature threshold of graphite. Phosphorus combustion chambers six meters in diameter by eleven meters in height (8) have been built using cemented graphite block construction.

The resistance of graphite to thermal shock, its stability at high temperatures, and its resistance to corrosion permit its use as self-supporting vessels to contain reactions at elevated temperatures (800–1700°C), eg, self-supporting reaction vessels for the direct chlorination of metal and alkaline-earth oxides. The vulnerability of cemented joints in these applications requires close tolerance ($\pm$0.10 mm) machining, a feat easily accomplished on graphite with conventional metal machining equipment.

Carbon Raschig-ring tower packing is available in sizes of 10–77 mm diameter. Bubble-cap trays, up to 3 m diameter for hydrochloric–organic stripping towers, and packing support structures, up to 5.5 m diameter for scrubbing towers in pulp and paper mill liquor recovery processes, have been installed. Because none of these components requires complex machining or a high degree of imperviousness, carbon rather than graphite is often used in these applications because of its lower cost.

Impervious Graphite. For applications where fluids under pressure must be retained, impregnated materials are available (6). Imperviousness is attained by blocking the pores of the graphite or carbon material with thermosetting resins such as phenolics, furans, and epoxies. Because the resin pickup is relatively small (usually 12–15 wt %), the physical properties exhibited by the original graphite or carbon material are retained. However, the flexural and compressive strengths are usually doubled. Graphite is also made impervious in a vacuum impregnation process.

Because carbon is difficult to machine, very little impervious carbon equipment is made. However, impervious graphite has been accepted as a standard material of construction by the chemical process industry for the fabrication of process equipment, such as heat exchangers, pumps, valves, towers, pipe, and fittings (9,10).

Many types of impervious graphite shell and tube, cascade, and immersion heat exchangers are in service throughout the world (11). The most common is the shell and tube design where an impervious graphite tube bundle with fixed and floating covers is employed in combination with a steel shell. Whenever parts must be joined, such as the tube to the tube sheet in a shell and tube heat exchanger, very thin resin cement joints are used. These resin cements have the same corrosion-resistant characteristics as the resins used to impregnate the graphite. Because of the high thermal conductivity of graphite, heat exchangers fabricated of impervious graphite have thermal efficiencies equal to metal heat exchangers of equivalent heat-transfer area. Heat exchangers up to 1.8 m diameter with areas up to 1300 m^2 are commercially available with operating pressures to 690 kPa (100 psi) and temperatures up to 170°C (12–14) (see HEAT EXCHANGE TECHNOLOGY).

Impervious graphite shells and tubes are used in numerous applications for transferring thermal energy, for example, boiling, cooling, or condensing. Large units are used extensively for cooling–condensing wet sulfur dioxide gas in sulfuric acid production plants that burn sludge acid (7).

Graphite heat exchangers are also used for evaporation of phosphoric acid and rayon spin bath solution; cooling electrolytic copper cell liquor; heating pickle liquor used for descaling sheet steel; boiling, heating, cooling, and absorbing hydrochloric acid and hydrogen chloride; and in many heating and cooling applications involving chlorinated hydrocarbons and sulfuric acid.

Impervious graphite heat exchangers machined from solid blocks are also available (15,16). The solid block construction is less susceptible to damage by mechanical shock, such as steam and water hammer, than are shell and tube exchangers. Block exchangers are limited in size and cost from 50–100% more than shell and tube units on an equivalent area basis.

Impervious graphite centrifugal pumps, pipe fittings, and valves were developed because most chemical processes require the movement of liquids. Graphite pipe and fittings in sizes ranging from 25 to 635 mm ID are used to convey corrosive fluids.

Towers, entrainment separators, thermowells, and rupture disks are fabricated of impervious graphite material. Many equipment items are available from stock. Special equipment can be custom-designed and built, and both standard and special items can be integrated to handle a complete process step. Systems for the absorption of hydrogen chloride in water to produce hydrochloric acid use impervious graphite equipment throughout. Usually, absorption is done in a falling-film absorber (17), a special design adaption of the shell and tube heat exchanger. This approach to absorption of hydrogen chloride (18) was developed and expanded in the United States and is now accepted as the standard.

Stripping hydrogen chloride (15–21) from aqueous hydrochloric acid and the subsequent production of anhydrous hydrogen chloride can be efficiently and economically achieved with a series of impervious graphite shell and tube heat exchangers that operate as falling-film reboiler, water and brine-cooled condensers, and bottoms acid cooler. In plants with available chlorine and hydrogen, the production of hydrogen chloride in any form or concentration can be achieved in a system that combines the burning of hydrogen in chlorine in a water-cooled graphite combustion chamber; absorption is carried out in an impervious graphite falling-film absorber, and a train of impervious graphite exchangers is used for stripping and drying (22).

Low Permeability Graphite. Most resin-impregnated impervious graphite materials have a maximum operating temperature limit of 170°C because of resin breakdown above this temperature. Certain special grades with a temperature limitation of 200°C are on the market (23). The chemical industry has developed high temperature processes (370°C and above) where equipment corrosion is a serious problem. Graphite equipment could solve the corrosion problem, but complete fluid containment is usually needed. To meet this need, graphite manufacturers have developed low permeability graphite materials where permeability is reduced by deposition of carbon and graphite in the pores of the base material (23). This material is not limited in its operating temperature, except in oxidizing conditions, and it is used to fabricate high temperature interchanger ejectors, fused salt cells, fused salt piping systems, and electric resistance heaters.

Porous Graphite. Several grades of low density, porous carbon and graphite are commercially available. A controlled combination of high

permeability and porosity characterizes these materials. Average pore diameters for typical grades are 0.03–0.12 mm with a total porosity of 48%. Porous graphite is manufactured by graphitizing the amorphous material.

Porous carbon and graphite are used in filtration of hydrogen fluoride streams, caustic solutions, and molten sodium cyanide; in diffusion of chlorine into molten aluminum to produce aluminum chloride; and in aeration of waste sulfite liquors from pulp and paper manufacture and sewage streams.

Mechanical Applications

Carbon–graphite possesses lubricity, strength, dimensional stability, thermal stability, and ease of machining, a combination of properties that has led to its use in a wide variety of mechanical applications for supporting rotating or sliding loads in contact. Its principal applications are in bearings, seals, and vanes, which are in sliding contact with a partner material. Mechanical applications of ccarbon–graphite include face, ring, and circumferential seals for gases and fluids both corrosive and noncorrosive; carbon cages for roller and ball bearings, carbon sleeve bearings and bushings, carbon thrust bearings or washers, and combination sleeve thrust bearings; packing rings for steam and water valve shafts and packing rings for compressor tail rods; and nonlubricated compressor parts such as piston rings, wear rings, segments, scuffer shoes, shaft tail-rod packing rings, pistons, and piston skirts. Miscellaneous applications include flat-plate slider parts for supporting machinery and facilitating sliding movement under load; and rotor vanes and metering device parts.

Carbon–graphite materials employed for mechanical applications are prepared by mixing selected sizes and types of carbon and graphite with binder materials such as pitches and resins. The mixtures are formed into compacts and baked to temperatures of ca 1000–3000°C. Specific raw materials and processing techniques are employed to obtain desired properties for the finished carbon–graphite materials (24).

The successful application of carbon–graphite as a sliding contact depends on the proper use of additives and impregnants in the carbon–graphite materials. Carbon–graphite, long considered to be self-lubricating, depends on the presence of adsorbed films of water vapor and or oxygen for its low friction and low wear properties. This adsorbed boundary layer is soon lost when the operation is conducted at high altitude, high temperature, or in cold, dry air. A substitute boundary layer can be formed by incorporating additives such as metallic sulfides, oxides, and halides, and impregnants such as thermoplastic and thermosetting resins. Additives and impregnants also serve to improve oxidation resistance, provide impermeability to high pressure gases and liquids, and even permit operation under high vaccum conditions (25), a primary requirement of equipment used for exploring outer space.

Carbon–graphite materials do not gall or weld even when rubbed under excessive load and speed. Early carbon materials contained metal fillers to provide strength and high thermal conductivity, but these desirable properties can now be obtained in true carbon–graphite materials that completely eliminate the galling tendency and other disadvantages of metals.

Electrode Applications

With the exception of carbon use in the manufacture of aluminum, the largest use of carbon and graphite is as electrodes in electric-arc furnaces. In general, the use of graphite electrodes is restricted to open-arc furnaces of the type used in steel production; whereas, carbon electrodes are employed in submerged-arc furnaces used in phosphorus, ferroalloy, and calcium carbide.

Graphite Electrodes. Graphite electrodes are commercially produced in many sizes ranging from 32 mm diameter by 610 mm length to 700 mm diameter by 2800 mm length, each diameter generally being available in two or three lengths. Such electrodes are used in open-arc furnaces for the manufacture of steel (26), iron and steel castings, brass, bronze, copper and its alloys, nickel and its alloys, magnesium, lead, tin, fused cast refractories, fused refractory grain, mineral wool insulation (27), and the treatment of toxic wastes (28). By far the largest use of graphite electrodes is in the manufacture of steel and, as a consequence, the growth of graphite production has been closely related to the growth in electric furnace steel production. Figure 3 is a schematic of a typical three-phase alternating current open-arc furnace, and shows the position of the three graphite electrode columns in this type furnace. A small but growing number of arc furnaces now use direct current and a single-electrode column positioned in the center of the furnace. In either case, steel is produced by filling the cylindrical shell with ferrous scrap, direct reduced iron, or occasionally, molten pig iron, then melting and refining the metallic charge with the intense heat derived from the electric arc generated at the tips of the electrodes.

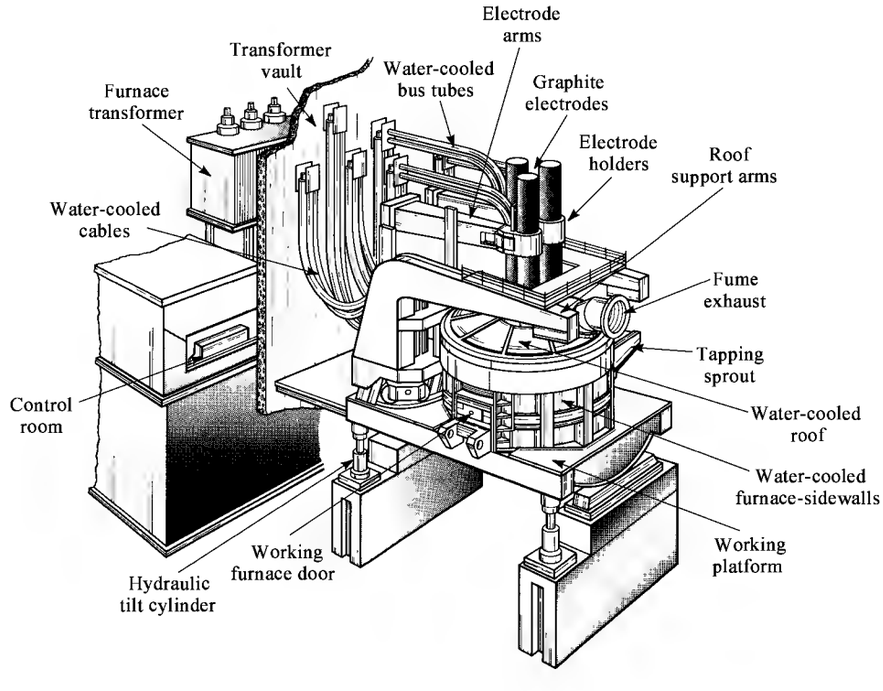

Fig. 3. Schematic of an electric-arc furnace. Courtesy of UCAR Carbon Technology Corp.

Prior to the mid-1940s, the arc furnace was used almost exclusively for the production of low tonnage, high quality steels such as stainless and alloy steels. Since then, its use has been extended to production of the more common high tonnage steel grades, including sheet steels (see STEEL). Domestic growth of arc furnace steel production has been dramatic, rising from 6% of total steel production in 1950, to 20% in 1975, and to 36% in 1990. Over 210 million metric tons of steel were produced in 1990 in electric-arc furnaces worldwide (29), approximately 26% of total world steel production, and these furnaces consumed over 800,000 tons of graphite electrodes (see FURNACES, ELECTRIC-ARC FURNACES).

Graphite electrodes are consumed in the melting process. For iron and steel production, the average consumption is ca 2–5 kg t, depending on the

quality of the charge material, the quality of the electrodes, and numerous factors related to the productivity and operation of the arc furnace (30). A combination of these factors has resulted in a reduction of about 40% in specific electrode consumption over the past 15 years. Electrode consumption can be classified into three broad categories: tip consumption, sidewall consumption, and breakage. Roughly half of the observed consumption occurs at the electrode tip where the intensely hot and rapidly moving arc spot produces both vaporization of the graphite and some ejection of small graphite particles. In addition, the electrode tip is eroded by contact with the liquid steel and slag. For a given electrode size, the rate of incremental tip consumption increases proportionally to the power and the square of the operating current (31). As a consequence, modern high power arc furnaces operate with high voltage, low current arcs in order to minimize electrode consumption. The periphery or sidewall of the hot electrode is slowly consumed by reaction with oxidizing atmospheres both inside and outside the furnace, resulting in tapering of the electrode toward the arc tip. Sidewall consumption is time dependent and is lowest for high productivity furnaces. Certain fume removal systems and the use of oxygen in the furnace for assisting melting and refining may increase sidewall consumption. Since sidewall consumption may account for 40% or more of total electrode consumption, extensive efforts have been made to reduce this component of consumption. Oxidation retardants, electrode coatings, and water-spray rings have been moderately successful in minimizing sidewall oxidation of the portion of the electrode outside the furnace. However, the extreme thermal and chemical environment inside the furnace has prevented to date similar reduction in sidewall consumption of electrodes once inside the furnace. A third form of consumption consists primarily of electrode breakage resulting from excessive movement of large masses of scrap during melting or the presence of nonconductors in the charge. Although such breakage generally accounts for less than 5% of net electrode consumption, excessive thermal shock, improper joining practices, excessive electrode column vibration, incorrect phase rotation, and inappropriate power programs can magnify this form of electrode consumption (30). Although attempts have been made to correlate electrode consumption with relatively small changes in electrode properties, the significant reductions in electrode consumption achieved make it clear that charge quality, furnace productivity, and furnace operating practices exert a more profound influence on electrode performance. Most notable is the established inverse relationship between furnace productivity and electrode consumption.

As the electrode is consumed from the tip, the periodic addition of electrodes to the top of the columns becomes necessary. In most domestic steel plants, electrode additions are made on top of the furnace without removing the electrode columns. In certain countries, however, the electrode columns are removed from the furnace, and electrode additions are made in an assembly station adjacent to the furnace. A typical electrode column contains two full-length electrodes plus a portion of a third electrode that is partially consumed.

Two configurations are in common use today for joining graphite electrodes. Both use tapered components with a thread pitch of either three or four threads per inch (2.54 cm). Electrodes of up to about 300 mm diameter frequently have one end machined with an external tapered male thread, whereas the other end contains an internally threaded female tapered socket. Two electrodes are joined by screwing the male end of one electrode into the female socket of the second electrode and applying the desired tightening torque. The more common system of joining electrodes is illustrated in Figure 4. In this case, an externally threaded, double-tapered connecting pin is used in conjunction with electrodes which have internally threaded tapered sockets in both ends. Prior to joint assembly, the connecting pin is screwed into the lower socket of the electrode to be added. This electrode is then raised, and the assembly screwed into the open socket of the other electrode on the furnace and torqued tight. Most electrode manufacturers now preset the connecting pin in one socket of each electrode prior to shipment in order to minimize potential electrode joining difficulties. National Electrical Manufacturers Association standards have been established for electrode sizes and for electrode socket and connecting pin configurations, sizes, and tolerances (32) in order to assure the interchangeability of electrodes and connecting pins from different manufacturers.

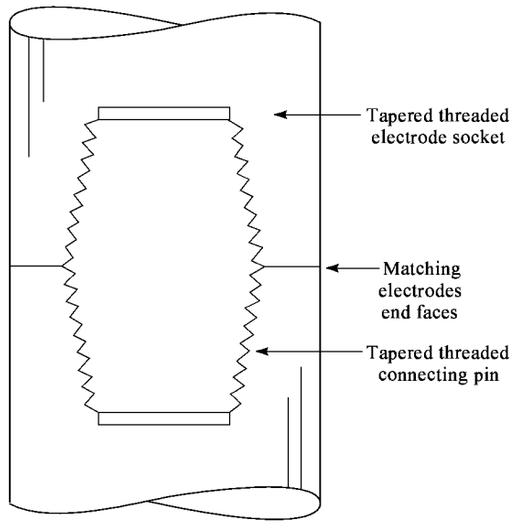

Fig. 4. Illustration of the use of a double-tapered connecting pin to join electrodes.

Graphite electrodes are produced in two broad-grade classifications, regular-grade and premium-grade. Typical room temperature properties of these grades are given in Table 2. The principal differences between the two grades are that the premium-grade is made from a superpremium needle coke and is pitch-impregnated prior to graphitization. The premium-grade electrode is used where very high performance is required, such as in the ultrahigh powered arc furnaces. The current-carrying capacity of an electrode column depends on many characteristics of the furnace operation as well as the characteristics of the electrode and electrode joint. Over the years, significant progress has been achieved in improving the current-carrying capacity of electrode columns. For example, the 510 mm diameter electrode first introduced in 1938 was designed to carry 26,000 A; this same size electrode carried 45,000 A by 1961, 55,000 A by 1975, and >60,000 A by 1990. Such improvements stem primarily from improved raw materials and process technology advancements that are not fully reflected in changes in electrode properties.

Table 2. Typical Room Temperature Properties of Regular- and Premium-Grade Graphite Electrodes and Connecting Pins

Property[a]	Regular-grade electrodes	Premium-grade electrodes	Premium-grade connecting pins
bulk density, g cm^{3}	1.60	1.70	1.80
resistivity, $\mu\Omega$·m	7.3	5.5	4.2
flexural strength, kPa[b]			
wg[b]	6,900	9,100	20,000
cg	5,800	7,000	12,500
elastic modulus, GPa[b]			
wg	5.3	7.6	17

cg	3.5	5.0	6.9
coefficient of thermal expansion (CTE), 10^{-6} °C			
wg	0.60	0.40	0.30
cg	1.40	1.10	2.20
thermal conductivity, W (m·K)[c]			
wg	134	168	180
cg	67	101	110
thermal shock parameter[d]			
wg	290×10^3	490×10^3	700×10^3
cg	80×10^3	130×10^3	90×10^3

[a] wg = with-grain; cg = cross-grain.

[b] To convert Pa to psi, multiply by 1.45×10^{-4}.

[c] Measured.

[d] Thermal shock parameter = $\frac{\text{thermal conductivity} \times \text{strength}}{\text{CTE} \times \text{elastic modulus}}$

In service, graphite electrodes operate at up to 2500 K and are subject to large thermal and mechanical stresses and extreme thermal shock. Graphite is unique in its ability to function in this extreme environment. The relatively low electrical resistance along the length of the electrode minimizes the power loss owing to resistance heating and helps keep the electrode temperature as low as possible. This characteristic is most important in ultrahigh power furnaces where the approximately 30% lower electrode resistivity of premium-grade electrodes is usually essential for successful operation. A high value of the thermal shock parameter is also important (Table 2); this parameter is improved by high strength and high thermal conductivity combined with low elastic modulus and low coefficient of thermal expansion. The ability of graphite electrodes to withstand thermal shock has been increased significantly in the past decade as a consequence of enhancement in the elastic modulus and coefficient of thermal expansion resulting from improved raw materials and advanced manufacturing technology.

The joints between electrodes are an extremely important part of the electrode system, both from the standpoint of resisting the mechanical forces of scrap caves and of carrying high electrical current density without localized overheating. To assure high mechanical and electrical performance of joints, electrode manufacturers carefully control the axial and radial thermal expansion characteristics of both the electrodes and the connecting pins, as well as the machining tolerances, in order to achieve the desired level of thermal tightening of the joint as the electrode column is heated in service. Such joints should possess high strength, especially in flexure, and possess very low electrical contact resistance. Careful assembly and proper torque are vital to good performance of electrode joints (30).

Carbon Electrodes. Carbon electrodes are rigid carbonaceous shapes deployed in electric furnaces. They are the final link in the chain of conductors from the energy source to the reaction zone of an electrically heated vessel. The gap bridged by the electrode is that between the contact plates that transmit current to the electrode and the discharge area at the arc end of the electrode.

Two types of carbon electrodes are in widespread use. Prebaked carbon electrodes (Fig. 5) are those made from a mixture of carbonaceous particles and a coal-tar pitch binder. The electrode is formed by extrusion or molding from a heated plasticlike mix and subsequently baked. Final bake temperature is sufficient to carbonize the binder, ie, about 850°C. At this temperature the binder is set, all volatiles have left, and a significant portion of the product shrinkage has occurred.

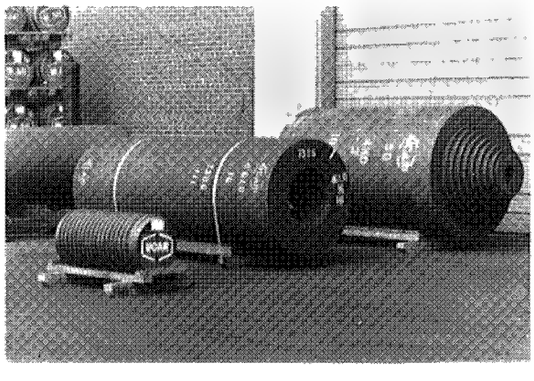

Fig. 5. Prebaked electrodes. Courtesy of UCAR Carbon Technology Corp.

Self-baked carbon electrodes are those whose shapes are formed *in situ* (33). The carbonaceous mixture is placed into a hollow tube-shaped metal casing. The upper end receives the unbaked mixture as a solid block, small particles, or warm plastic paste. The casing contains inwardly-projecting longitudinal perforated fins that become surrounded by baked carbon as the casing is incrementally moved downward and through the contact plates. Casing and carbon are consumed in this furnace.

Several systems are under development that will reduce or negate casing movement with the carbon (34–36). These will be more acceptable to furnace processes where product contamination by the casing material is undesirable.

Two types of furnaces use carbon electrodes. In the open-arc the raw materials fed into the furnace do not contact the electrode. An arc is maintained between the electrode and the charged material or the liquid bath that results from melting the charge. A furnace producing molten steel from a charge of solid metallic scrap is an example of an open-arc. The development of graphite electrodes has practically eliminated carbon electrodes from most open-arc units. The graphite can conduct much more current per unit of cross-sectional area and use of carbon in modern high powered open-arc systems is not a practical choice. Carbon is still the electrode of choice for certain open-arc furnaces such as those that produce refractories and those utilized in slag cleaning facilities.

Submerged-arc furnaces are the other type of equipment using carbon electrodes. In these, the charge materials are in contact with the electrodes. Some of the energy imparted from the electrode may be in the form of an arc to the charge or to the bath. It also may flow between electrodes through a conductive charge. Submerged-arc furnaces are quiet because the sound generated by the arc is attenuated by the covering burden of charge material.

A variety of products are made in submerged-arc furnaces. Among them are various alloys and compounds. Each uses a particular type or grade of carbon electrode to hold production costs at the lowest possible level. Graphite electrodes could be and are used in some submerged-arc furnaces. Such a choice is the result of special conditions that warrant use of the more expensive graphite in lieu of carbon.

Ferroalloy and carbide producers are the largest volume users of carbon electrodes. These are the self-baking type and ferrosilicon is the dominant product. Prebaked cathodes are used to produce silicon where a low iron content in the metal is required. A typical open top submerged-arc furnace is shown in Figure 6. Two silicon grades dominate the market; chemical-grade for producing silicones, and metallurgical-grade for alloying with aluminum. Another important use of prebakes is in the production of thermal phosphorus to be used for the manufacture of high purity phosphoric acid. These

furnaces are sealed. A typical phosphorus furnace is shown in Figure 7.

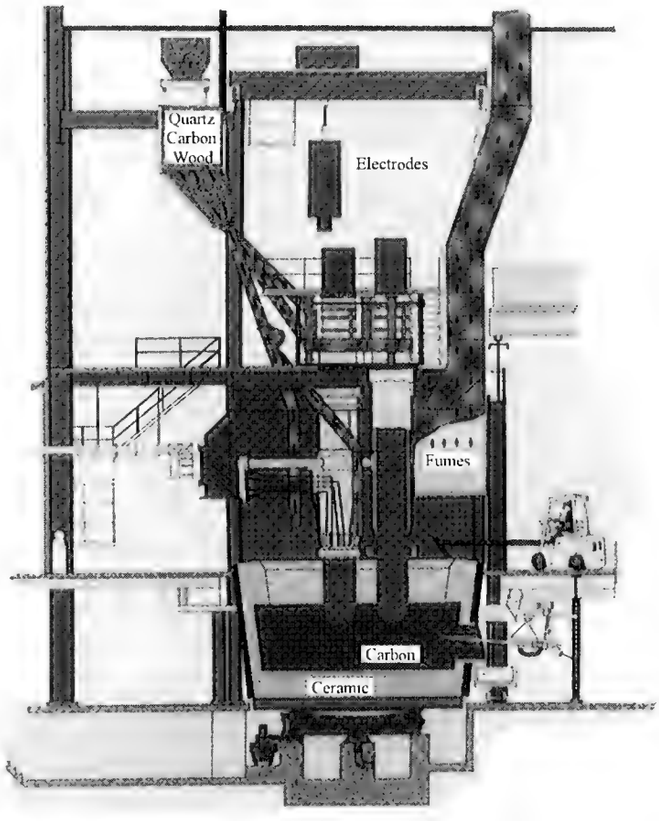

Fig. 6. Typical silicon metal furnace. Courtesy of UCAR Carbon Technology Corp.

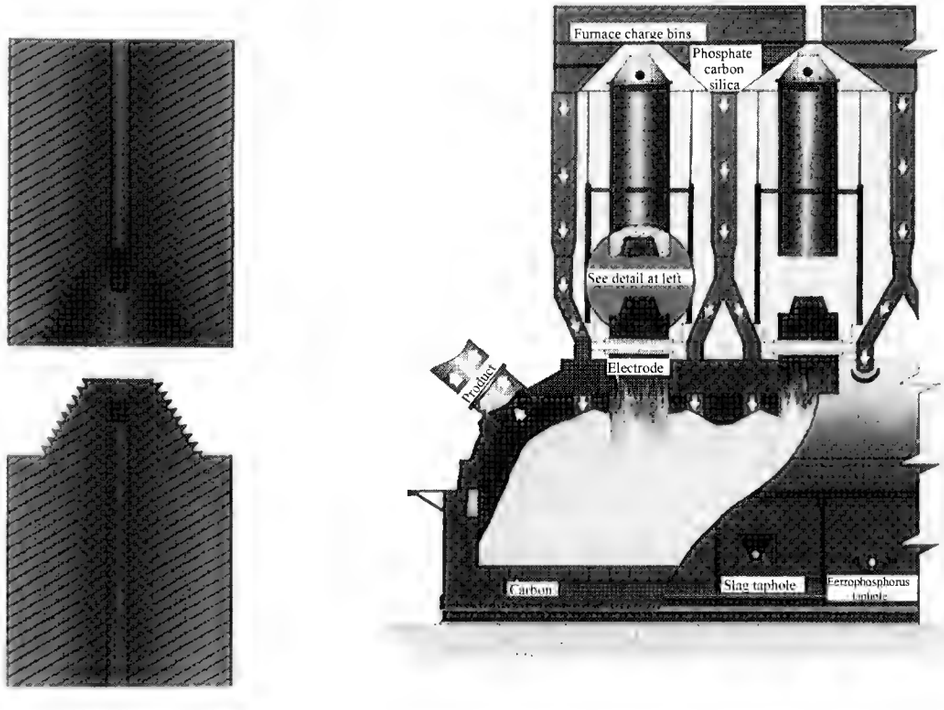

Fig. 7. Typical phosphorus furnace. Courtesy of UCAR Carbon Technology Corp.

Several grades of carbon electrodes are available. The characteristics of each result from the raw materials and processes used in manufacturing. The generic descriptions and primary constituents are as follows:

Coal electrodes	The primary constituent is calcined anthracite coal particles.
Coke electrodes	The primary constituent is calcined petroleum coke particles.
Semigraphite electrodes	The primary constituent is sized graphite particles.
High purity electrodes	The final product has a low ash and/or low iron content achieved by raw material selection or special processing.

All carbon electrodes are amorphous. They are formed from a mixture of particles, fillers, and a binder, and they are baked to about 850°C. This is

not high enough to cause the development of a crystalline structure as would occur if the temperature was elevated to that needed for graphitization.

Prebaked carbon electrodes are manufactured in all diameters up through 1500 mm. Some prebakes are produced as quadriforms to suit specific furnaces. Self-baking electrodes are in service through 2134 mm diameter. Electrode lengths are as needed for particular applications. Rounds are available in lengths up to 2794 mm and quadriforms as long as 3556 mm. Self-baked electrodes are continuous.

Production of carbon electrodes is a capital-intensive business. Two suppliers dominate the prebaked market. Carbon paste producers are more numerous and tend to serve local markets. There is no international standard for the threaded joints on carbon electrodes. Manufacturers of straight pin carbon electrodes have followed the physical specifications adopted for graphite electrodes (37). Unified standards do not exist for pinless joints resulting in limited interchangeability among brands. Electrode diameters are offered in both English and metric sizes with no restrictions on new or unique diameters.

The physical properties of carbon electrodes are determined by the raw materials and processes used in their manufacturer. There are no universal grade designations and the published properties are quite broad. Table 3 shows ranges for some of the common commercially available grades.

Table 3. Ranges of Physical Properties of Typical Carbon Electrode Grades

Property	Range
apparent density, g mL	1.50–1.68
specific resistance, $\mu\Omega$·m	21–50
flexural strength, MPa[a]	3.1–6.9
Young's modulus, GPa	4.1–8.8
ash content, wt %	0.6–8.0

[a] To convert MPa to psi, multiply by 145.

The density, flexural strength, and electrical conductivity increase with greater amounts of graphite particles in the mix. Flexural strength and Young's modulus move together. Ash increases in proportion to the amount of coal in the mix. Higher graphite content increases the electrode cost. Users select that electrode which gives the lowest bottom line cost per unit of production. The stated properties cannot be equated to performance. The user needs to resolve the overall performance in actual production to determine the best grade for the specific application.

All electrodes pass through the contact pads of the electrode holder and terminate some distance above the furnace hearth. As it is consumed, the electrode is slipped downward. Self-baked electrodes are continuous and the slipping rate can be only as rapid as baking allows. Prebaked rounds are connected axially one to another with threaded features (Fig. 8). A carbonaceous connecting pin, usually made of graphite, is threaded into sockets in the ends of two axially aligned electrodes. Forming a male (external) thread on one electrode permits its connection into a threaded female (internal) socket on the other electrode. Quadriform electrodes are firmly connected to the source of power and are suspended, keeping the electrode vertical in the furnace. When the usable length of the quadriform is consumed, the remainder of the electrode is removed and replaced with full-length stock. One form of the noncircular electrode is called a packet. A few packet furnaces are still in operation.

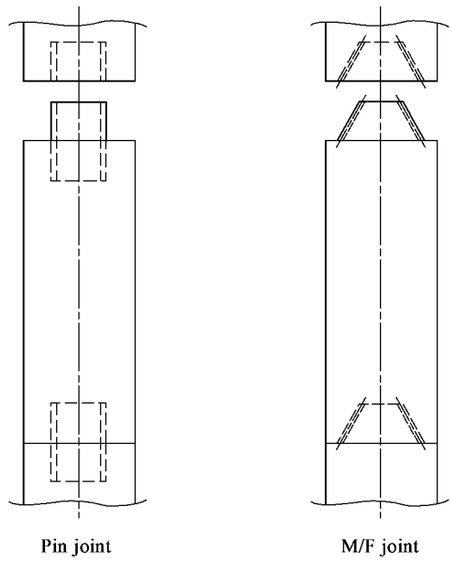

Fig. 8. Prebaked electrode joints. Courtesy of UCAR Carbon Technology Corp.

There is no limit to the possible configurations of electric furnaces. They exist as single-phase or polyphase, a-c or d-c, and one to six or more electrodes. The furnace cross sections can be round, heart-shaped, oval, rectangular, or variations of each. Some furnaces, especially those for silicon production, have a rotating hearth and shell.

Carbon electrodes are the normal choice for the link in the connection chain to deliver power to the arc tip. Graphite may be used in special applications, but the higher cost of graphite favors the use of carbon electrodes. Carbon possesses properties ideal to its application as an electrode. These properties include no softening point, no melting point, electrical conductivity, strength increases with increasing temperature, resistivity drops as temperature increases, available in the size and purity desired, and cost effectiveness.

Pin-type electrode connections are engineered to perform across a wide temperature range. Thermal tightening is a feature that causes increasing unit contact pressure on the end faces and the contacting thread flanks. Axial CTE of the carbon is greater than the axial CTE of the pin. Transverse CTEs are controlled to either add to or not detract from the axial tightening effect. The magnitude of the thermal tightening is often such that permanent tensile elongation occurs in the pin and permanent compressive deformation occurs at the end faces. As a result, the joint will open when it is cooled sufficiently, because the elastic limits of the pin and electrodes had been exceeded.

The mechanisms of electrode consumption are dictated by the environment in which the electrode operates. Oxidation occurs on those surfaces exposed to oxygen when they are above the oxidation threshold temperature. Erosion removes carbon as it is abraded through its contact with the charge material or from movement of the electrode in the burden. The electrode is constantly repositioned in the axial direction as necessary to maintain a desired arc length. Part of the tip losses result from sublimation. At the tip there is particle loss resulting from the detonation effect of an alternating current arc. A portion of the electrode enters the electro-thermal reduction process. The electrode becomes a reductant if the charge mixture is carbon "short," ie, less than stoichiometric. The loss of large or massive amounts follows column breakup from cracks and splits in the structure or from a full break across the

electrode cross section.

Self-baking carbon electrode columns have longitudinal fissures. This results from melting or oxidation of the casing fins that extend inwardly from the casing. These fissures act as crack stoppers, but they also generate additional exposed area for oxidation. Joints in prebaked electrode columns that do not remain tight become open at the end faces. Socket splitting and cross cracks usually occur. If these joints survive to the arc region, the splits and cracks can propagate and cause chunking of the carbon. These rather large pieces are undesirable for several reasons. They can upset the reaction in progress at the arc tip, they are a cause of inefficient electrode utilization, and they may foul tap holes thereby impeding proper furnace operation.

The demand for self-baking carbon electrodes is keyed to the steel industry since it is the principal consumer of ferroalloys. Demand for prebaked electrodes is predicted to grow through the year 2000 at an annual rate of about 5% . The demand for chemical-grade silicon is the driving force for this growth. Production of metallurgical-grade has a positive but lower growth rate than that for chemical-grade silicon. Usage in production of elemental thermal phosphorus is predicted to be stable since improvements in the wet acid process can supply the increasing demand for high purity phosphoric acid.

Although carbon electrode production has been regarded as a mature business, the steady growth in demand and the need for improved electrodes has prompted ongoing development efforts in these areas: (*1*) cost containment through raw material substitutions and process improvements; (*2*) higher purity electrodes for those processes such as silicon production; (*3*) improvements in thermal shock resistance to enhance electrode performance; and (*4*) better joining systems for prebakes.

Anode Applications. Graphite has been used as the primary material for electrolysis of brine (aqueous) and fused-salt electrolytes, both as anode and cathode. Technological advances, however, have resulted in a dimensionally stable anode (DSA) consisting of precious metal oxides deposited on a titanium substrate that has replaced graphite as the primary anode (38–41) (see ALKALI AND CHLORINE PRODUCTS).

The cell is the basis of all electrolysis. The anode admits current into the electrolyte and the cathode serves as a means of exit for the electrical current. The electrical flow provides a definition for electrolysis: the flow of current from the anode through the electrolyte and out of the cell through the cathode with ensuing decomposition of the electrolyte, with products being formed at the electrodes.

Graphite properties conducive to successful electrolytic application include high electrical conductivity, high degree of insolubility and operation at low voltage, high purity, low initial cost, easily machinable, and few limitations as to size and shape.

The service life of graphite anodes largely depends on three factors: (*1*) electrochemical attack by nascent oxygen, resulting from oxidation at the surface; (*2*) chemical attack through the chemical reaction of cell products; and (*3*) mechanical loss of material as a result of (*1*) and (*2*). Although the eventual service life is limited by these three factors, it is not uncommon for graphite anodes to provide 300–700 days of service life. Anode operating life is also influenced by a number of cell operating variables, such as cell temperature, brine flow rate, brine concentration, and the current density imposed on the anode.

The two basic types of graphite anodes used are plain and impregnated. Impregnation prevents anolyte penetration of the graphite pores and resultant corrosion from within. For impregnated anodes, base graphites with initial porosities of 15 to 30% are given a vacuum-pressure impregnation usually with an oil, such as linseed, to fill or coat the accessible pores. For some low temperature electrolysis applications, resin treatments such as phenolics are used. These applications are well below the temperature limitations of these resins. Proper impregnation provides a 25 to 50% increase in anode life over unimpregnated graphite.

Chemical Production. Electrolytic production of chemicals is conducted either by solution (water) electrolysis or fused-salt electrolysis. Fluorine, chlorine, chlorate, and manganese dioxide are liberated from water solutions; magnesium and sodium are generated from molten salt solutions.

Fluorine. This application uses carbon plates as the anode in a fluorine salt solution. Since the ordered crystal structure of graphite results in short life, carbon is the preferred anode material (see FLUORINE).

Chlorine. Most processors have converted from graphite to metal anodes. The two basic designs were diaphragm cells, which used graphite plates as anodes, and mercury cells in which a layer of mercury acted as the cathode with intricately machined graphite blocks as the anode (42).

Chlorate. Conversion to metal anodes has also taken place in this process. Sodium hydroxide, which is formed at the cathode, reacts to form the sodium chlorate product (see ALKALI AND CHLORINE PRODUCTS).

Manganese Dioxide. Graphite plates used as anodes in this process are coated with MnO_2 during electrolysis. The anodes are removed from the solution periodically and the MnO_2 is removed by mechanical methods. Graphite can also be used as the cathode material. Titanium is used as anode materials where high quality MnO_2 is desired.

Magnesium. This molten salt electrolysis process is the current principal method of magnesium production. The graphite anodes can be either round or rectangular in nature (see MAGNESIUM AND MAGNESIUM ALLOYS).

Sodium. In this process, sodium is produced from molten salt. Individual cells are made up of a number of large round anodes (25–50 cm diameter) and steel pipe cathodes (see SODIUM AND SODIUM ALLOYS).

Cathodic Protection. Another application for graphite anodes is for cathodic protection. All metal structures placed on or underground are subject to corrosion by galvanic action. Current flow, either localized or general, results in oxidation, ie, rusting, of steel. Graphite anodes are used for impressed current protection and a current is induced in the circuit counter to the galvanic current. Since the polarity is reversed, the steel does not corrode. The graphite is normally impregnated with linseed oil resin impregnates to enhance life and an electrical connection is made inside the anode with a copper wire that is ultimately connected to steel to be protected. Life of the anode can range from 3–30 years in cathodic protection applications (43,44).

The low cost, light weight, and excellent electrical conductivity of graphite anodes have made this impressed current protection system valuable for cathodic protection of pipelines, storage vessels, process equipment, and also for well casings both on- and offshore.

Metallurgical Applications

Because of their unique combination of physical and chemical properties, manufactured carbons and graphites are widely used in several forms in high temperature processing of metals, ceramics, glass, and fused quartz. A variety of commercial grades is available with properties tailored to best meet the needs of particular applications (45). Industrial carbons and graphites are available in a broad range of shapes and sizes.

Structural Graphite Shapes. In many metallurgical and other high temperature applications, manufactured graphite is used because it neither melts nor fuses to many common metals or ceramics, exhibits increasing strength with temperature, has high thermal shock resistance, is nonwarping, has low expansion, and possesses high thermal conductivity. However, because of its tendency to oxidize at temperatures above 750 K, prolonged exposure at higher temperatures frequently necessitates use of a nonoxidizing atmosphere. In addition, prolonged contact both with liquid steel and with liquid metals that rapidly form carbides should be avoided.

Some of the more common applications for structural graphite shapes are (*1*) hot-pressing molds and dies (46) for beryllium at 1370 K and 6.9 MPa (1000 psi); diamond-impregnated drill bits and sawtooth segments at 1250 K and 13.8 MPa (2000 psi); tungsten and other refractory metals and alloys up to 2370 K and 6.9 MPa (1000 psi); and boron nitride and boron carbide up to 2060 K; (*2*) molds for metal casting steel railroad car wheels made by the controlled-pressure pouring process (47); steel slabs and billets made by the controlled-pressure pouring process (48); continuous casting of copper and its alloys, aluminum and its alloys, bearing materials; zinc and its alloys; and gray iron (49,50); centrifugal casting of brasses, bronzes, steels, and refractory metals (51); nickel anodes; welding rods and thermite welding molds; shapes of refractory metals (Ti, Zr, Mo, Nb, and W) and carbides; and shapes of gray, ductile and malleable irons (52); (*3*) foundry accessories including: mold chill plates, core rods, and riser rods; crucible skimmer floats; plunging bells for magnesium additions to ductile iron and desulfurization of blast-furnace hot metal (53,54); stirring rods for nonferrous metals; and railroad brake shoe inserts; (*4*) injection tubes and nozzles for purifying molten aluminum (55) and other nonferrous metals, desulfurization of blast furnace and foundry iron with calcium carbide or magnesium, and carbon raising of foundry iron with graphite powders; (*5*) aluminum extrusion components including dies, guides from die openings, run-out table boards, and cooling-rack inserts; (*6*) rolls for handling metal sheets are used in certain processes because they are self-lubricating and reduce surface marring; (*7*) immersion thermocouple protection tubes for nonferrous metals; (*8*) welding electrodes for welding, gouging, and cutting iron and steel, particularly with the aid of an air blast (56); (*9*) crucibles, either induction or resistance heated, for producing tungsten carbide, beryllium fluoride and beryllium, titanium and zirconium fluoride, semiconductor crystals germanium and silicon, and for laboratory chemical

analysis equipment; (*10*) ceramic and glass production including: inserts for glass bottle takeout holders, casting molds for fused-cast refractories of alumina, magnesium, and chrome–magnesite composition up to 2650 K (57); mold susceptors for fabricating fused magnesia crucibles; susceptors, electrical resistor elements, fusion crucibles, molds and dies for the production of fused quartz (58); linings for float-glass plate production; and linings for hydrofluoric acid tanks for glass etching; (*11*) boats, trays, and plates for sintering clutch plates, brake disks, and cemented carbides and for the manufacture of semiconductor material and transistors; (*12*) furnace jigs for brazing honeycomb panels, automotive ignition points and arms, automotive radiator cores, transistor junction assemblies, and glass-to-metal seals; and (*13*) tooling for forming high temperature composite resin system aircraft parts (59).

Electric Heating Elements. Machined graphite shapes are widely used as susceptors and resistor elements to produce temperatures up to 3300 K in applications utilizing nonoxidizing atmospheres. The advantages of graphite in this type of application include its very low vapor pressure (lower than molybdenum), high black body emissivity, high thermal shock resistance, and increasing strength at elevated temperatures with no increase in brittleness. Graphites covering a broad range of electrical resistivity are available and can be easily machined into complex shapes at lower cost than refractory metal elements. Flexible graphite cloth is also used widely as a heating element since its low thermal mass permits rapid heating and cooling cycles. Typical applications include molten-iron or steel-holding furnaces, continuous casting tundishes, liquid–steel degassing units, chemical reaction chambers, quartz-fusion apparatus, zinc-vaporization chambers, sintering furnaces, vapor deposition units (qv) (60,61), and single-crystal silicon ingot growing furnaces (Czochralski method). In the furnaces that use vacuum or inert gas atmospheres, porous carbon or graphite, flexible carbon or graphite felts, and rigid fibrous graphite thermal insulation materials are extensively used.

Carbon and Graphite Powder and Particles. Manufactured graphite powders and particles are used extensively in metallurgical, chemical, and electrochemical applications where the uniformity of physical and chemical characteristics, high purity, and rapid solubility in certain molten metals are important factors (62). The many grades of carbon and graphite powders and particles are classified on the basis of fineness and purity. Applications for these materials include facings for foundry molds and steel ingot molds; additives to molten iron to control carbon level and chill characteristics; covering material for molten nonferrous metals and salt baths to prevent oxidation; additives to sintered materials to control carbon level and frictional characteristics; additions in oil, grease-, and oil-less bearings; oil well drill bit lubricant; and as charge-carbon and slag foaming agents in steel made in electric arc furnaces. The electrical and thermal conducting characteristics of carbon and graphite powders and particles account for their use as additives in dry cell batteries, paint, thermoset polybutadiene composites (63), ground anode backfill, concrete and corrosion-resistant sulfur concrete.

Refractory Applications

Various forms of carbon, semigraphite, and graphite materials have found wide application in the metals industry, particularly in connection with the production of iron, aluminum, and ferroalloys. Carbon has been used as a refractory material since 1850, though full commercial acceptance and subsequent rapid increase in use has occurred only since 1945.

Carbon as a Blast Furnace Refractory. The first commercial use of carbon as a refractory for a blast furnace lining took place in France in 1872, followed in 1892 by a carbon block hearth in a blast furnace of the Maryland Steel Co. at Sparrows Point, Maryland. After a period of abated interest the excellent results obtained with several carbon hearths in England, Germany, and the United States during the late 1930s and early 1940s, renewed enthusiasm for the material. Although initially used only for the hearth bottom of blast furnaces, carbon, semigraphite, semigraphitized carbon, and graphite refractories have been successfully applied to hearth walls, tuyere zones, boshes, and even the lower to midstack of modern, intensely cooled, high performance blast furnaces around the world (64). More than 400 individual carbon or graphite blast furnace linings have been installed in North America through mid-1990. Additionally, carbon has also been used extensively for iron trough, iron runner, and slag runner safety linings, especially when external cooling is employed to extend the life of the ceramic working linings.

Carbonaceous and graphitic materials possess important characteristics that make them ideal blast furnace refractories: (*1*) they do not soften or lose strength at high operating temperatures of approximately 1150–1200°C; (*2*) they resist attack by molten slag and iron; (*3*) their relatively high thermal conductivity, when combined with adequate cooling and proper design concepts, promotes the formation of solidified coatings of slag and iron on their hot face. These coatings prevent erosion from the molten materials and process gases, promoting long life (65); (*4*) they possess excellent resistance to thermal shock, preventing spalling and cracking which interrupts heat transfer to the cooling system and exposes more refractory surface area to chemical attack; (*5*) a positive, low coefficient of thermal expansion provides dimensional stability and tightening of joints in the multipiece linings. However, because of their relatively low threshold temperature for oxidation from steam, carbon dioxide, or air, care must be taken to limit their exposure to these elements and maintain proper cooling at all times, to minimize damage from these temperature-dependent reactions (66,67).

The prime requirement of any carbonaceous material used in the blast furnace hearth wall or bottom is to contain liquid iron and slag safely within the crucible, throughout extended periods of continuous operation, often up to 15 years.

This requirement is most readily achieved if the lining design concepts employed and the carbonaceous or graphitic materials utilized with these concepts, combine to provide a refractory mass free from cracking caused by mechanical and thermal stress (68). Additionally, the refractory materials must exhibit thermal conductivities that are high enough to permit the formation of solidifying layers of iron and slag on their hot faces and permeabilities that are low enough to prevent the impregnation of the refractories by alkalies and other process contaminants (69). It is also helpful if the refractory materials themselves are resistant to attack from alkalies by virtue of the inclusion of various additives during their manufacture (68). Proper cooling of the materials also contributes to their longevity.

For practical reasons, the blast furnace hearth is divided into two principal zones: the bottom and the sidewalls. Each of these zones exhibits unique problems and wear mechanisms. The largest refractory mass is contained within the hearth bottom. The outside diameters of these bottoms can exceed 16 or 17 m and their depth is dependent on whether underhearth cooling is utilized. When cooling is not employed, this refractory depth usually is determined by mathematical models; these predict a stabilization isotherm location which defines the limit of dissolution of the carbon by iron. Often, this depth exceeds 3 m of carbon. However, because the stabilization isotherm location is also a function of furnace diameter, often times thermal equilibrium cannot be achieved without some form of underhearth cooling.

This cooling can be accomplished by utilizing water, oil, induced or forced draft air, or passively, with a thick layer of high thermal conductivity graphite. The use of underhearth cooling not only allows a thermal equilibrium to be achieved but also permits a shallower depth of refractory to be used, reducing lining cost. The cooling system can employ a pipe system or airtight steel plenums (70).

The main mechanisms of hearth bottom wear are high heat load, chemical attack, erosion from molten liquids, mechanical and thermal stress, and penetration because of ferrostatic and process pressure. A variety of special purpose carbons have been developed to minimize or eliminate the damage caused by these wear mechanisms.

In North America the individual blocks of carbon used in the hearth bottom have exceeded 6 m in length. In Europe and Asia these blocks are much shorter because of manufacturing capabilities. The longer bottom blocks permit the spanning of the hearth diameter with only two pieces, which prevents flotation of the carbon by the denser molten iron. This is because the bearing provided by the dead load of the hearth walls, which rest on the ends of the carbon block "beams," anchors the bottom blocks and prevents flotation. If smaller blocks are utilized with two or more joints across the bottom, special reverse taper mating surfaces or interlocking techniques are required to prevent block flotation.

Occasionally the carbon bottom blocks in the lower most course are arranged vertically in "soldier block" fashion. The theory is that this arrangement permits the greatest heat-transfer capability of the material because of its anisotropy. Because these carbon blocks are usually extruded or pressed, there can be a 10% higher thermal conductivity in the direction perpendicular to the pressing direction and this practice takes advantage of this carbon characteristic. However, the vertical blocks in this configuration are more susceptible to differential temperature-induced stress and cracking. These designs are most prevalent in Russia and other Eastern European countries utilizing their technology.

The latest design philosophy is to utilize various types of ceramic refractories as the working lining on top of the carbon bottom. This relegates the carbon material in the bottom to a cooling function instead of a crucible function, since the molten liquids are contained completely within the ceramic layers. The high conductivity of the carbon or graphite used as the cooling layer permits thermal equilibrium to be achieved while the liquid iron is still within the ceramic. One European ironmaker has dispensed with all carbon in the hearth bottom and instead utilizes a graphite-cooled ceramic bottom,

promoting this concept worldwide.

The hearth wall zone of the blast furnace presents different design problems and exhibits different main mechanisms of wear. Because these linings must contain molten iron, water cooling must be maintained on the external furnace jacket, either utilizing flooded water jackets or spray showers or by the use of water-cooled, cast-iron stave coolers located within the vessel at the cold face of the refractories. Heat removal, therefore, must travel through the wall thickness to the cooling element. Thus the design concepts employed as well as the properties of the refractory utilized have a direct bearing on the success of the hearth wall.

In North America, a special, high conductivity, low permeability, "hot-pressed" carbon brick is utilized almost exclusively for hearth walls. Because of their relatively small size and special, heat setting resin cement, and because the brick is installed tightly against the cooled jacket or stave, differential thermal expansion can be accommodated without refractory cracking and effective cooling can be maintained. Additionally, the wall thickness is generally smaller than 1 m, which promotes the easy formation of a protective skull of frozen materials on its hot face. Thus hearth wall problems and breakouts because of carbon wall refractory failure are virtually nonexistent.

Elsewhere, large block carbons are utilized as wall material, generally with thicknesses in the range of 1.5–2.5 m. However, the single-thickness blocks have a tendency to crack and spall because of high mechanical and thermal stress and lack of expansion provisions. To combat this problem, various exotic carbons have been developed to resist hot metal penetration and increase thermal conductivities, but it should be noted that these measures do not solve the cause of the cracking, which is a lack of provisions to accommodate differential expansion.

Another problem inherent to large block designs is the fact that ramming materials must be utilized to fill the annulus that forms between the circular shell or staves and the large cross-section carbon block. Usually this annulus is 75–150 mm thick. The ramming materials used to fill this annulus always possess thermal conductivities that are severely affected by shrinkage of the ram, improper rammed density, deterioration over time because of contamination from leaking cooling water or the process environment. As a result, this rammed gap acts as a thermal barrier to effective heat transfer to the cooling system. The result is a higher carbon wall temperature with consequent accelerated wall wear.

This wear is caused primarily from high thermal and mechanical stress, chemical attack, attack by iron and slag, oxidation, and severe thermal shock. Thus the design of the hearth wall and the concepts employed are just as important as the carbon or graphite materials chosen for the refractory material. Despite their benefits and properties, no carbon or graphite material can overcome the problems of an improper hearth wall design concept.

In the early 1960s, the use of carbon and more recently, semigraphite and graphite as bosh refractories, has found increased acceptance and resulted in longer furnace campaign life. As is the case in the hearth wall, long life is dependent on efficient cooling of the carbonaceous or graphitic material. Originally, all carbon materials were cooled on their cold face, either by external shell spray cooling or external water jackets. Later, cast-iron, water-cooled staves were successfully used to cool the cold face of the bosh wall. However, all of these cooling systems required that the heat travel completely through the wall to reach the cooling element. These cooling methods were employed as a result of the high risk of water leaks because of poor quality coolers. These leaks could prove disastrous because the leaking water and consequential steam would badly oxidize the surrounding carbon. However, dramatic improvements in copper cooling plate technology and casting practice and sophisticated water leak detection systems have combined to provide low risk, high efficiency, inserted copper cooler systems for carbonaceous or graphitic linings. This results in lower refractory temperatures and, thus, lower chemical attack from alkalies, which are temperature-dependent reactions with carbon (71).

These advances in cooling technology have also provided an opportunity to extend the thermal shock and chemical resistance of graphitic materials above the bosh, into the blast furnace stack. It has been recognized by many blast furnace operators around the world that the most destructive wear mechanism in the upper bosh and lower to midstack level is thermal shock. It is also universally recognized that the only refractory material that can withstand the magnitude of the temperature peaks normally occurring in these blast furnace zones are graphitic in nature. Therefore, the combination of densely spaced, modern copper coolers with high quality semigraphite or graphite refractories has proven to be a successful extender of blast furnace campaign life (72). Several furnaces have recently been relined utilizing these concepts in Holland, Canada, Italy, and the United States; several others are planned in England and Central America. As a result, the percentage of carbonaceous and graphitic materials utilized in the blast furnace is increasing tremendously and this trend should continue into the late 1990s.

Refractories for Cupolas. In many ways, the use of carbon cupola linings has paralleled the application of carbon in the blast furnace. Carbon brick and block are used to line the cupola well (73) or crucible. When properly installed and cooled carbon linings last for many months or even years of intermittent operation. Their resistance to molten iron and both acid and basic slags provides not only insurance against breakouts but also operational flexibility to produce different iron grades without the necessity of changing refractories. Carbon is also widely used for the tap hole blocks, breast blocks, slagging troughs, and dams.

Refractories for Electric Reduction Furnaces. Carbon hearth linings are used in submerged-arc, electric-reduction furnaces producing phosphorus, calcium carbide, all grades of ferrosilicon, high carbon ferrochromium, ferrovanadium, and ferromolybdenum. Carbon is also used in the production of beryllium oxide and beryllium copper where temperatures up to 2273 K are required.

The principles pertaining to carbon blast furnace hearths apply as well to submerged-arc furnace hearths. In some processes, such as in d-c arc furnaces, the electrical conductance of carbon is a most important factor. The long life of carbon linings in these applications is attributable to carbon's exceptional resistance to corrosive slags and metals at very high temperatures.

Refractories in the Aluminum Industry. Carbon materials are used in the Hall-Heroult primary aluminum cell as anodes, cathodes, and sidewalls because of the need to withstand the corrosive action of the molten fluorides used in the process (see ALUMINUM AND ALUMINUM ALLOYS). Production of one metric ton of molten aluminum requires about 500 kg of anode carbon and 7.5–10 kg of cathode blocks which is the largest industry usage of carbon materials. Aluminum smelters generally have an on-site carbon plant for anode production. Anode technology is focused on raw materials (petroleum coke and coal-tar pitch), processing techniques, and rodding practices (74).

Prebaked cathode blocks used today are electrically calcined anthracite coal, semigraphite, semigraphitized, or graphite composition (75). Desired cathode operating characteristics include resistance to sodium attack, high operating strength, low porosity, high thermal shock resistance, and low electrical resistance. The use of graphitic prebaked cathode blocks is a balance among performance, power, life, and economics within the cell; coal-based carbon is still the predominant cathode block composition. Cathode technology developments include coatings of titanium diboride (76) for voltage reduction and cemented collector bar assembly practices (77).

Sidewall blocks are monolithic rammed carbon or prebaked carbon and graphite blocks. Thermal conductivity to maintain a ledge against the molten metal is the most significant sidewall operating parameter. Some pots utilize both carbon and graphite sidewall blocks to maximize performance in specific sidewall areas. Thermal shock resistance and strength are also desired sidewall properties. Low temperature resin cast carbon, ie, cold-cast materials, can also be used for corner block locations. Carbonaceous cements and pastes are used for joint integrity and thermal balance.

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OTHER FORMS OF CARBON AND GRAPHITE

The versatility and uniqueness of carbon and graphite attest to its widespread use for a variety of industrial applications. Several other forms of graphite (1), which have not been fully exploited, are characteristically high in cost but their properties are intriguing enough that applications are continually being found, resulting in further development of new emerging industries.

Flexible Graphite

A useful form of graphite is a flexible sheet or foil. Because of graphite's stability at high temperatures, flexible foil is useful in applications requiring thermal stability in corrosive environments, eg, gaskets and valve packings, and is often used as a replacement for asbestos gaskets. The basic structure of flexible graphite results in both mechanical and sealing characteristics (2) without additives, a decisive advantage over contemporary facing materials which are more dependent on binders and impregnants to generate adequate properties.

A common method of manufacturing flexible graphite (3) involves treating natural graphite flake with an oxidizing agent such as a solution of nitric and sulfuric acid to form an intercalated compound with graphite. Upon heating at high temperature, the intercalants in the graphite crystal form a gas that causes the layers of the graphite to separate and the graphite flakes to expand or exfoliate in an accordionlike fashion in the *c*-direction, ie, the direction perpendicular to the crystalline planes of the graphite. The expanded flakes are then compressed into sheets which are flexible and can be formed and cut into various shapes. Improvements in the process for reducing material and production costs (4) have been reported.

Carbon and Graphite Foam

Carbon–graphite foam is a unique material that has yet to find a place among the various types of commercial specialty graphites. Its low thermal conductivity, mechanical stability over a wide range of temperatures from room temperature to 3000°C, and light weight make it a prime candidate for thermal protection of new, emerging carbon–carbon aerospace reentry vehicles.

The open cell structure of carbon foam with its greater than 90% porosity and chemical inertness at temperatures below 500°C suggests its use as a filtration media for corrosive liquids and a dispersant for gases.

The earliest foamed graphite was made from exfoliated small crystals of graphite bound together and compacted to a low density (5–7). This type of foam is structurally weak and will not support loads of even a few newtons per square meter. More recently, carbon and graphite foams have been produced from resinous foams of phenolic or urethane base by careful pyrolysis to preserve the foamed cell structure in the carbonized state. These foams have good structural integrity, eg, a typical foam of 0.25 g/cm^3 apparent density has a compressive strength of 9.3–15 MPa (1350–2180 psi) with thermal conductivity of 0.87 W/(m·K) at 1400°C. These properties make the foam attractive as a high temperature insulating packaging material in the aerospace field and as insulation for high temperature furnaces (see INSULATION, THERMAL). Variations of the resinous-based foams include the syntactic foams where cellular polymers or hollow carbon spheres comprise the primary volume of the material bonded and carbonized in a resin matrix.

Pyrolytic Graphite

Pyrolytic graphite was first produced in the late 1800s for lamp filaments. Today, it is produced in massive shapes, used for missile components, rocket nozzles, and aircraft brakes for advanced high performance aircraft. Pyrolytic graphite coated on surfaces or infiltrated into porous materials is also used in other applications, such as nuclear fuel particles, prosthetic devices, and high temperature thermal insulators.

Of the many forms of carbon and graphite produced commercially, only pyrolytic graphite (8,9) is produced from the gas phase via the pyrolysis of hydrocarbons. The process for making pyrolytic graphite is referred to as the chemical vapor deposition (CVD) process. Deposition occurs on some suitable substrate, usually graphite, that is heated at high temperatures, usually in excess of 1000°C, in the presence of a hydrocarbon, eg, methane, propane, acetylene, or benzene.

The largest quantity of commercial pyrolytic graphite is produced in large, inductively heated furnaces in which natural gas at low pressure is used as the source of carbon. Deposition temperatures usually range from 1800 to 2000°C on a deposition substrate of fine-grain graphite.

The properties of pyrolytic graphite exhibit a high degree of anisotropy. For example, the tensile strength in the *ab* direction is five to ten times greater than that of conventional graphite and the strength in the *c* direction is proportionately lower. Similarly, the thermal conductivity of pyrolytic graphite in the *ab* direction ranks among the highest of elementary materials, whereas in the *c* direction its thermal conductivity is quite low. At room temperature, the thermal conductivity values in the *ab* direction are three hundred times greater than in the *c* direction. Pyrolytic graphite with a density of 2.0–2.1 g/cm^3 is the most dense of the commercially produced graphites, exhibiting low porosity and low permeability.

A special form of pyrolytic graphite is produced by annealing under pressure at temperatures above 3000°C. This pressure-annealed pyrolytic graphite exhibits the theoretical density of single-crystal graphite, and though the material is polycrystalline, the properties of the material are close to single-crystal properties. The highly reflective, flat faces of pressure-annealed pyrolytic graphite have made the material valuable as an x-ray monochromator (see X-RAY TECHNOLOGY).

Glassy Carbon

Glassy, or vitreous, carbon is a black, shiny, dense, brittle material with a vitreous or glasslike appearance (10,11). It is produced by the controlled pyrolysis of thermosetting resins; phenol–formaldehyde and polyurethanes are among the most common precursors. Unlike conventional artificial graphites, glassy carbon has no filler material. The liquid resin itself becomes the binder.

There is little crystal growth during carbonization, which always occurs in the solid phase. The solid cross-linking that occurs at this time does not lend itself to crystal growth. The glassy carbons are composed of random crystallites of the order of 5.0 nm across and are not significantly altered by ordinary graphitization heat treatment to 2800°C.

The properties of glassy carbon are unlike those of conventional carbon and graphites. Exhibiting a density of 1.4–1.5 gm/cm^3, they have low open porosity and low permeability. The hardness and brittleness of this material is the same as that of ordinary glass. Chemical inertness and low permeability have made glassy carbon a useful material for chemical laboratory crucibles and other vessels. It is used as a container/heater for the epitaxial growth of silicon crystals and as crucibles for the growth of single crystals. Also, this type of carbon is useful for metallurgical crucibles (12), heating elements, heat-resistant tubes, machine parts, and electrical parts.

Carbon and Graphite Paper

Carbon and graphite paper is produced from carbon fibers by conventional papermaking methods. The carbon or graphite fibers are cut or chopped to a

size suitable for processing, about one-fourth inch in length, homogeneously intermixed with water and a starch binder to form an aqueous slurry, and then deposited from the slurry on a substrate to form a sheet. The sheet is then processed by conventional papermaking techniques to produce a carbon or graphite paper.

This form of carbon and graphite has outstanding electrical conductivity, corrosion resistance, and moderately high strength. These properties have promoted its use in electrodes for electrostatic precipitators. Composites made of laminated carbon paper (13) are excellent high temperature thermal insulators, having a thermal conductivity of less than 1.4 W (m·K) (0.8 (BTU·ft) (ft^2·h·°F)) at room temperature. The material is not substantially affected by being subjected to high temperature. The thermal conductivity increases to 0.5 W (m·K) (0.3 (BTU·ft) (ft^2·h·°F)) at 2000°C, but is still significantly low, particularly in view of its low density (0.5 g mL).

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ACTIVATED CARBON

Activated carbon is a predominantly amorphous solid that has an extraordinarily large internal surface area and pore volume. These unique characteristics are responsible for its adsorptive properties, which are exploited in many different liquid- and gas-phase applications. Activated carbon is an exceptionally versatile adsorbent because the size and distribution of the pores within the carbon matrix can be controlled to meet the needs of current and emerging markets (1). Engineering requirements of specific applications are satisfied by producing activated carbons in the form of powders, granules, and shaped products. Through choice of precursor, method of activation, and control of processing conditions, the adsorptive properties of products are tailored for applications as diverse as the purification of potable water and the control of gasoline emissions from motor vehicles.

In 1900, two very significant processes in the development and manufacture of activated carbon products were patented (2). The first commercial products were produced in Europe under these patents: Eponite, from wood in 1909, and Norit, from peat in 1911. Activated carbon was first produced in the United States in 1913 by Westvaco Corp. under the name Filtchar, using a by-product of the papermaking process (3). Further milestones in development were reached as a result of World War I. In response to the need for protective gas masks, a hard, granular activated carbon was produced from coconut shell in 1915. Following the war, large-scale commercial use of activated carbon was extended to refining of beet sugar and corn syrup and to purification of municipal water supplies (4). The termination of the supply of coconut char from the Philippines and India during World War II forced the domestic development of granular activated carbon products from coal in 1940 (5). More recent innovations in the manufacture and use of activated carbon products have been driven by the need to recycle resources and to prevent environmental pollution.

Physical and Chemical Properties

The structure of activated carbon is best described as a twisted network of defective carbon layer planes, cross-linked by aliphatic bridging groups (6). X-ray diffraction patterns of activated carbon reveal that it is nongraphitic, remaining amorphous because the randomly cross-linked network inhibits reordering of the structure even when heated to 3000°C (7). This property of activated carbon contributes to its most unique feature, namely, the highly developed and accessible internal pore structure. The surface area, dimensions, and distribution of the pores depend on the precursor and on the conditions of carbonization and activation. Pore sizes are classified (8) by the International Union of Pure and Applied Chemistry (IUPAC) as micropores (pore width <2 nm), mesopores (pore width 2–50 nm), and macropores (pore width >50 nm) (see ADSORPTION).

The surface area of activated carbon is usually determined by application of the Brunauer-Emmett-Teller (BET) model of physical adsorption (9,10) using nitrogen as the adsorptive (8). Typical commercial products have specific surface areas in the range 500–2000 m^2 g, but values as high as 3500–5000 m^2 g have been reported for some activated carbons (11,12). In general, however, the effective surface area of a microporous activated carbon is far smaller because the adsorption of nitrogen in micropores does not occur according to the process assumed in the BET model, which results in unrealistically high values for surface area (10,13). Adsorption isotherms are usually determined for the appropriate adsorptives to assess the effective surface area of a product in a specific application. Adsorption capacity and rate of adsorption depend on the internal surface area and distribution of pore size and shape but are also influenced by the surface chemistry of the activated carbon (14). The macroporosity of the carbon is important for the transfer of adsorbate molecules to adsorption sites within the particle.

Functional groups are formed during activation by interaction of free radicals on the carbon surface with atoms such as oxygen and nitrogen, both from within the precursor and from the atmosphere (15). The functional groups render the surface of activated carbon chemically reactive and influence its adsorptive properties (6). Activated carbon is generally considered to exhibit a low affinity for water, which is an important property with respect to the adsorption of gases in the presence of moisture (16). However, the functional groups on the carbon surface can interact with water, rendering the carbon surface more hydrophilic (15). Surface oxidation, which is an inherent feature of activated carbon production, results in hydroxyl, carbonyl, and carboxylic groups that impart an amphoteric character to the carbon, so that it can be either acidic or basic. The electrokinetic properties of an activated carbon product are, therefore, important with respect to its use as a catalyst support (17). As well as influencing the adsorption of many molecules, surface oxide groups contribute to the reactivity of activated carbons toward certain solvents in solvent recovery applications (18).

In addition to surface area, pore size distribution, and surface chemistry, other important properties of commercial activated carbon products include pore volume, particle size distribution, apparent or bulk density, particle density, abrasion resistance, hardness, and ash content. The range of these and other properties is illustrated in Table 1 together with specific values for selected commercial grades of powdered, granular, and shaped activated carbon products used in liquid- or gas-phase applications (19).

Table 1. Properties of Selected U.S. Activated Carbon Products[a]

Property	Manufacturer Precursor Product grade Product form Typical range	Gas-phase carbons Calgon Coal BPL Granular	Norit Peat B4 Extruded	Westvaco Wood WV-A 1100 Granular	Liquid-phase carbons Calgon Coal SGL Granular	Norit Peat SA 3 Powdered	Westvaco Wood SA-20 Powdered
particle size, U.S. mesh[b,c]	<4	12 × 30	3.8 mm	10 × 25	8 × 30	64% < 325	65–85% < 325
apparent density, g cm^3	0.2–0.6	>0.48	0.43	0.27	0.52	0.46	0.34–0.37
particle density, g cm^3	0.4–0.9	0.80		0.50	0.80		
hardness number	50–100	>90	99				
abrasion number					>75		
ash, wt %	1–20	<8	6		<10	6	3–5
BET surface area, N_2, m^2 g	500–2500	1050–1150	1100–1200	1750	900–1000	750	1400–1800
total pore volume, cm^3 g	0.5–2.5	0.8	0.9	1.2	0.85		2.2–2.5
CCl_4 activity, wt %	35–125	>60					
butane working capacity, g 100 cm^3	4–14			>11.0			
iodine number	500–1200	>1050			>900	800	>1000
decolorizing index Westvaco	15–25						>20

molasses number				
Calgon	50–250		>200	
Norit	300–1500			440
heat capacity at 100°C, J (g·K)[d]	0.84–1.3	1.05	1.05	
thermal conductivity, W (m·K)	0.05–0.10			

[a] Specific values shown are those cited in manufacturers' product literature (19). Typical ranges shown are based on values reported in the open literature.

[b] Unless otherwise noted.

[c] Approximate mm corresponding to cited meshes are mesh: mm—4: 4.76; 8: 2.38; 10: 2; 12: 1.68; 25: 0.72; 30: 0.59; 325: 0.04.

[d] To convert J to cal, divide by 4.184.

Manufacture and Processing

Commercial activated carbon products are produced from organic materials that are rich in carbon, particularly coal, lignite, wood, nut shells, peat, pitches, and cokes. The choice of precursor is largely dependent on its availability, cost, and purity, but the manufacturing process and intended application of the product are also important considerations. Manufacturing processes fall into two categories, thermal activation and chemical activation. The effective porosity of activated carbon produced by thermal activation is the result of gasification of the carbon at relatively high temperatures (20), but the porosity of chemically activated products is generally created by chemical dehydration reactions occurring at significantly lower temperatures (1,21).

Thermal Activation Processes. Thermal activation occurs in two stages: thermal decomposition or carbonization of the precursor and controlled gasification or activation of the crude char. During carbonization, elements such as hydrogen and oxygen are eliminated from the precursor to produce a carbon skeleton possessing a latent pore structure. During gasification, the char is exposed to an oxidizing atmosphere that greatly increases the pore volume and surface area of the product through elimination of volatile pyrolysis products and from carbon burn-off. Carbonization and activation of the char are generally carried out in direct-fired rotary kilns or multiple hearth furnaces, but fluidized-bed reactors have also been used (22). Materials of construction, notably steel and refractories, are designed to withstand the high temperature conditions, ie, >1000°C, inherent in activation processes. The thermal activation process is illustrated in Figure 1 for the production of activated carbon from bituminous coal (23,24).

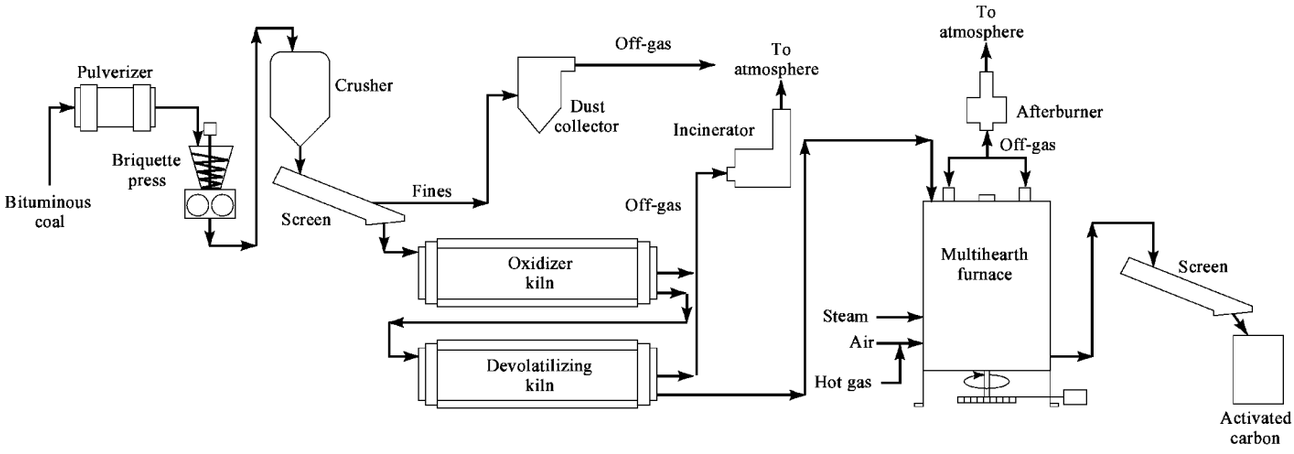

Fig. 1. Thermal activation of bituminous coal.

Bituminous coal is pulverized and passed to a briquette press. Binders may be added at this stage before compression of the coal into briquettes. The briquetted coal is then crushed and passed through a screen, from which the on-size material passes to an oxidizing kiln. Here, the coking properties of the coal particles are destroyed by oxidation at moderate temperatures in air. The oxidized coal is then devolatilized in a second rotary kiln at higher temperatures under steam. To comply with environmental pollution regulations, the kiln off-gases containing dust and volatile matter pass through an incinerator before discharge to the atmosphere.

The devolatilized coal particles are transported to a direct-fired multihearth furnace where they are activated by holding the temperature of the furnace at about 1000°C. Product quality is maintained by controlling coal feed rate and bed temperature. As before, dust particles in the furnace off-gas are combusted in an afterburner before discharge of the gas to the atmosphere. Finally, the granular product is screened to provide the desired particle size. A typical yield of activated carbon is about 30–35% by weight based on the raw coal.

The process for the thermal activation of other carbonaceous materials is modified according to the precursor. For example, the production of activated carbon from coconut shell does not require the stages involving briquetting, oxidation, and devolatilization. To obtain a high activity product, however, it is important that the coconut shell is charred slowly prior to activation of the char. In some processes, the precursor or product is acid-washed to obtain a final product with a low ash content (23,25).

Chemical Activation Processes. In contrast to the thermal activation of coal, chemical activation is generally carried out commercially in a single kiln. The precursor, usually wood, is impregnated with a chemical activation agent, typically phosphoric acid, and the blend is heated to a temperature of 450–700°C (26). Chemical activation agents reduce the formation of tar and other by-products, thereby increasing carbon yield. The chemical activation process is illustrated in Figure 2, for the production of granular activated carbon from wood (23,27).

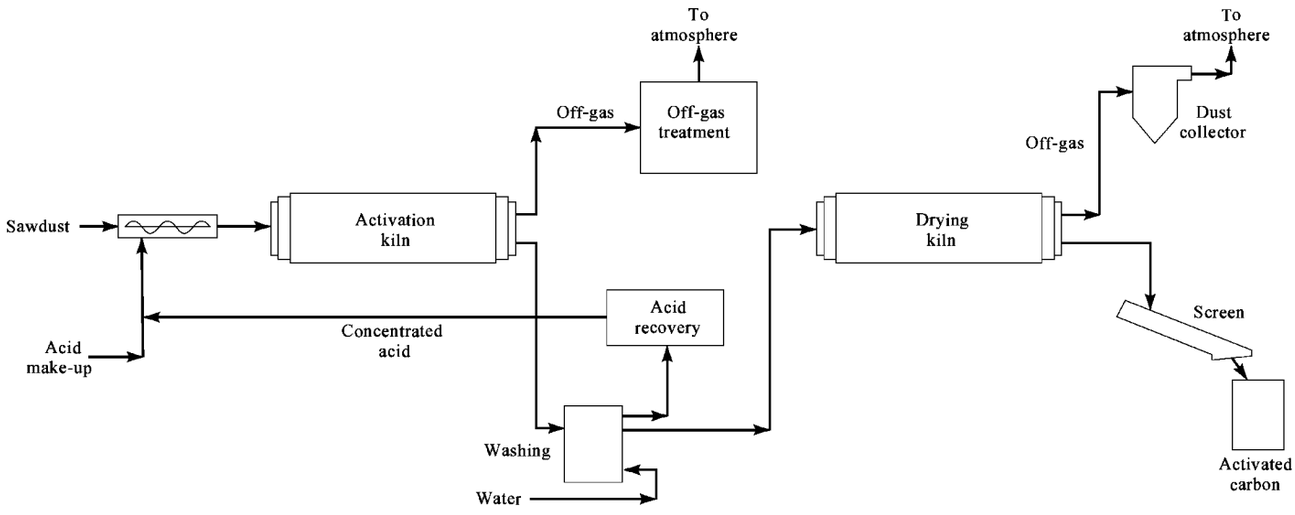

Fig. 2. Chemical activation of wood.

Sawdust is impregnated with concentrated phosphoric acid and fed to a rotary kiln, where it is dried, carbonized, and activated at a moderate temperature. To comply with environmental pollution regulations, the kiln off-gases are treated before discharge to the atmosphere. The char is washed with water to remove the acid from the carbon, and the carbon is separated from the slurry. The filtrate is then passed to an acid recovery unit. Some manufacturing plants do not recycle all the acid but use a part of it to manufacture fertilizer in an allied plant. If necessary, the pH of the activated carbon is adjusted, and the product is dried. The dry product is screened and classified into the size range required for specific granular carbon applications. Carbon yields as high as 50% by weight of the wood precursor have been reported (26).

Novel Manufacturing Processes. Different chemical activation processes have been used to produce carbons with enhanced adsorption characteristics. Activated carbons of exceptionally high surface area (>3000 m^2 g) have been produced by the chemical activation of carbonaceous materials with potassium hydroxide (28,29). Activated carbons are also produced commercially in the form of cloths (30), fibers (31), and foams (32) generally by chemical activation of the precursor with a Lewis acid such as aluminum chloride, ferric chloride, or zinc chloride.

Forms of Activated Carbon Products. To meet the engineering requirements of specific applications, activated carbons are produced and classified as granular, powdered, or shaped products. Granular activated carbons are produced directly from granular precursors, such as sawdust and crushed and sized coconut char or coal. The granular product is screened and sized for specific applications. Powdered activated carbons are obtained by grinding granular products. Shaped activated carbon products are generally produced as cylindrical pellets by extrusion of the precursor with a suitable binder before activation of the precursor.

Shipping and Storage. Activated carbon products are shipped in bags, drums, and boxes in weights ranging from about 10 to 35 kg. Containers can be lined or covered with plastic and should be stored in a protected area both to prevent weather damage and to minimize contact with organic vapors that could reduce the adsorption performance of the product. Bulk quantities of activated carbon products are shipped in metal bins and bulk bags, typically 1–2 m^3 in volume, and in railcars and tank trucks. Bulk carbon shipments are generally transferred by pneumatic conveyors and stored in tanks. However, in applications such as water treatment where water adsorption does not impact product performance, bulk carbon may be transferred and stored as a slurry in water.

Specifications. Activated carbon producers furnish product bulletins that list specifications, usually expressed as a maximum or minimum value, and typical properties for each grade produced. Standards helpful in setting purchasing specifications for granular and powdered activated carbon products have been published (33,34).

Economic Aspects

Excluding Eastern European countries and China where production figures have not been published, the world production capacity of activated carbon was estimated to be 375,000 metric tons in 1990 (35). The price of most products was 0.70 to 5.50 $ kg, but some specialty carbons were more expensive (36). Forty percent of the production capacity was in the United States, 30% in Western Europe, 20% in Japan, and 10% in other Pacific Rim countries (Table 2).

Table 2. World[a] Production Capacity, Estimated 1990

Country	Capacity, 10^3 t
United States	146
Western Europe	108
Japan	72
Pacific Rim, other	49
Total	*375*

[a] Excluding Eastern Europe and China.

Production capacity was almost equally split between powdered and nonpowdered activated carbon products. Powdered activated carbon, a less expensive form used in liquid-phase applications, is generally used once and then disposed of. In some cases, however, granular and shaped products are regenerated and reused (35). In 1990 production capacity for granular and shaped products was split with about two-thirds for liquid-phase and one-third for gas-phase applications (37).

Over the last decade production capacity in the United States remained essentially unchanged, but minor fluctuations occurred in response to changes in environmental regulations (38). A similar reaction was noted worldwide (35). The current demand for activated carbon is estimated at 93% of production capacity. The near-term growth in demand is projected to be approximately 5.5% yr (39).

In 1970 the U.S. Congress enacted the Clean Air Act, the Clean Water Act, and the Safe Drinking Water Act. Because activated carbon can often be used to help meet Environmental Protection Agency (EPA) regulations, the U.S. activated carbon industry reacted by increasing its production capacity. A proposed amendment to the Safe Drinking Water Act in 1979 required the use of granular activated carbon systems, but the amendment was not enacted. In response to the projected increase in demand for activated carbon, production capacity remained high until the late 1980s, but when the anticipated need did not materialize, some production facilities were shut down. Currently, because of stricter EPA regulations implementing all three acts in 1990, the industry will increase production capacity by 25% during the next several years (35,40).

The estimated production capacity of activated carbon in the United States is shown in Table 3 for seven manufacturers (41). The principal producers are Calgon Carbon (37%), American-Norit (26%), Westvaco (19%), and Atochem (10%). Several other companies purchase activated carbon for resale but do not manufacture products.

Table 3. Production Capacity in the United States, Estimated 1990

Company	Location	Capacity, 10^3 t
Acticarb Division, Royal Oak Enterprises	Romeo, Fla.	6.8
American Norit Co.	Marshall, Tex.	38.6
Barneby and Sutcliffe	Columbus, Ohio	3.0
Calgon Carbon Corp.	Catlettsburg, Ky. and Pittsburgh, Pa.	53.5
Ceca Division, Atochem NA	Pryor, Okla.	15.0
Trans-Pacific Carbon	Blue Lake, Calif.	2.3
Westvaco Corp.	Covington, Va.	27.2
Total		*146.4*

Western Europe has seven manufacturers of activated carbon. The two largest, Norit and Chemviron (a subsidiary of Calgon), account for 70% of West European production capacity, and Ceca accounts for 13% (42). Japan is the third largest producer of activated carbon, having 18 manufacturers, but four companies share over 50% of the total Japanese capacity (43). Six Pacific Rim countries account for the balance of the world production capacity of activated carbon, 90% of which is in the Philippines and Sri Lanka (42). As is the case with other businesses, regional markets for activated carbon products have become international, leading to consolidation of manufacturers. Calgon, Norit, Ceca, and Sutcliffe-Speakman are examples of multinational companies.

Activated carbon is a recyclable material that can be regenerated. Thus the economics, especially the market growth, of activated carbon, particularly granular and shaped products, is affected by regeneration and industry regeneration capacity. The decision to regenerate an activated carbon product is dependent on the cost, size of the carbon system, type of adsorbate, and the environmental issues involved. Large carbon systems, such as those used in potable and wastewater treatment, generally require a high temperature treatment, which is typically carried out in rotary or multihearth furnaces. During regeneration, carbon losses of 1 to 15% typically occur from the treatment and movement of the carbon (44). However, material loss is compensated for by the addition of new carbon to the adsorber system. In general, regeneration of spent carbon is considerably less expensive than the purchase of new activated carbon. For example, fluidized-bed furnace regeneration of activated carbon used in a 94,600 m^3 per day water treatment system cost only 35% of new material (45). For this system, regeneration using either infrared or multihearth furnaces was estimated to be more expensive but still significantly less so than the cost of new carbon.

Because powdered activated carbon is generally used in relatively small quantities, the spent carbon has often been disposed of in landfills. However, landfill disposal is becoming more restrictive environmentally and more costly. Thus large consumers of powdered carbon find that regeneration is an attractive alternative. Examples of regeneration systems for powdered activated carbon include the Zimpro Passavant wet air oxidation process (46), the multihearth furnace as used in the DuPont PACT process (47,48), and the Shirco infrared furnace (49,50).

Other types of regenerators designed for specific adsorption systems may use solvents and chemicals to remove susceptible adsorbates (51), steam or heated inert gas to recover volatile organic solvents (52), and biological systems in which organics adsorbed on the activated carbon during water treatment are continuously degraded (53).

Analytical Test Procedures and Standards

Source references for frequently used test procedures for determining properties of activated carbon are shown in Table 4. A primary source is the *Annual Book of American Society for Testing and Materials (ASTM) Standards* (61). Other useful sources of standards and test procedures include manufacturers of activated carbon products, the American Water Works Association (AWWA) (33,34), and the Department of Defense (54).

Table 4. Source References for Activated Carbon Test Procedures and Standards

Title of procedure or standard	Source
Standard Definitions of Terms Relating to Activated Carbon	ASTM D2652
Apparent Density of Activated Carbon	ASTM D2854
Particle Size Distribution of Granular Activated Carbon	ASTM D2862
Total Ash Content of Activated Carbon	ASTM D2866
Moisture in Activated Carbon	ASTM D2867
Ignition Temperature of Granular Activated Carbon	ASTM D3466
Carbon Tetrachloride Activity of Activated Carbon	ASTM D3467
Ball-Pan Hardness of Activated Carbon	ASTM D3802
Radioiodine Testing of Nuclear-Grade Gas-Phase Adsorbents	ASTM D3803
pH of Activated Carbon	ASTM D3838
Determination of Adsorptive Capacity of Carbon by Isotherm Technique	ASTM D3860
Determining Operating Performance of Granular Activated Carbon	ASTM D3922
Impregnated Activated Carbon Used to Remove Gaseous Radio-Iodines from Gas Streams	ASTM D4069
Determination of Iodine Number of Activated Carbon	ASTM D4607
Military Specification, Charcoal, Activated, Impregnated	Ref. 54
Military Specification, Charcoal, Activated, Unimpregnated	Ref. 54
AWWA Standard for Granular Activated Carbon	Ref. 33
AWWA Standard for Powdered Activated Carbon	Ref. 34
BET Surface Area by Nitrogen Adsorption	Refs. 6, 8, 9, 55
Pore Volume by Nitrogen Adsorption or Mercury Penetration	Refs. 10, 56–59
Particle Density	Ref. 60

Health and Safety

Activated carbon generally presents no particular health hazard as defined by NIOSH (62). However, it is a nuisance and mild irritant with respect to inhalation, skin contact, eye exposure, and ingestion. On the other hand, special consideration must be given to the handling of spent carbon that may contain a concentration of toxic compounds.

Activated carbon products used for decolorizing food products in liquid form must meet the requirements of the *Food Chemical Codex* as prepared by the Food & Nutrition Board of the National Research Council (63).

According to the National Board of Fire Underwriters, activated carbons normally used for water treatment pose no dust explosion hazard and are not subject to spontaneous combustion when confined to bags, drums, or storage bins (64). However, activated carbon burns when sufficient heat is applied; the ignition point varies between about 300 and 600°C (65).

Dust-tight electrical systems should be used in areas where activated carbon is present, particularly powdered products (66). When partially wet activated carbon comes into contact with unprotected metal, galvanic currents can be set up; these result in metal corrosion (67).

Manufacturer material safety data sheets (MSDS) indicate that the oxygen concentration in bulk storage bins or other enclosed vessels can be reduced by wet activated carbon to a level that will not support life. Therefore, self-contained air packs should be used by personnel entering enclosed vessels where activated carbon is present (68).

Liquid-Phase Applications

Activated carbons for use in liquid-phase applications differ from gas-phase carbons primarily in pore size distribution. Liquid-phase carbons have significantly more pore volume in the macropore range, which permits liquids to diffuse more rapidly into the mesopores and micropores (69). The larger pores also promote greater adsorption of large molecules, either impurities or products, in many liquid-phase applications. Specific-grade choice is based on the isotherm (70,71) and, in some cases, bench or pilot scale evaluations of candidate carbons.

Liquid-phase activated carbon can be applied either as a powder, granular, or shaped form. The average size of powdered carbon particles is 15–25 μm (70). Granular or shaped carbon particle size is usually 0.3–3.0 mm. A significant factor in choosing between powdered and nonpowdered carbon is the degree of purification required in the adsorption application. Granular and shaped carbons are usually used in continuous flow through deep beds to remove essentially all contaminants from the liquid being treated. Granular and shaped carbon systems are preferred when a large carbon buffer is needed to withstand significant variations in adsorption conditions, such as in cases where large contaminant spikes may occur. A wider range of impurity removal can be attained by batch application of powdered carbon, and the powdered carbon dose per batch can be controlled to achieve the degree of purification desired (69) (see ADSORPTION, LIQUID SEPARATION).

Batch-stirred vessels are most often used in treating material with powdered activated carbon (72). The type of carbon, contact time, and amount of carbon vary with the desired degree of purification. The efficiency of activated carbon may be improved by applying continuous, countercurrent carbon–liquid flow with multiple stages (Fig. 3). Carbon is separated from the liquid at each stage by settling or filtration. Filter aids such as diatomaceous earth are sometimes used to improve filtration.

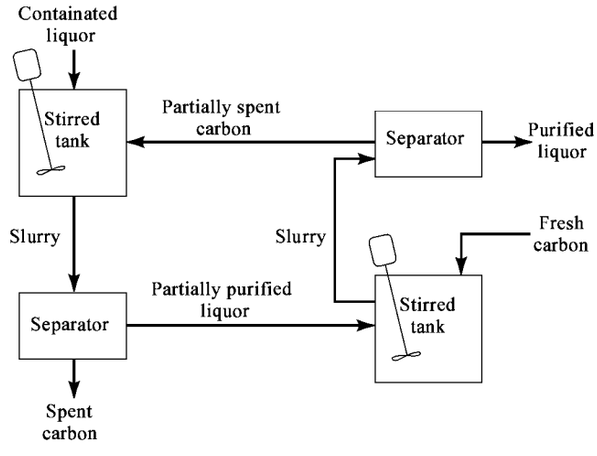

Fig. 3. Multistage countercurrent application of powdered activated carbon.

Granular and shaped carbons are used generally in continuous systems where the liquid to be treated is passed through a fixed bed (72,73). Compounds are adsorbed by the carbon bed in the adsorption zone (Fig. 4). As carbon in the bed becomes saturated with adsorbates, the adsorption zone moves in the direction of flow, and breakthrough occurs when the leading edge of the adsorption zone reaches the end of the column. Normally at least two columns in series are on line at any given time. When the first column becomes saturated, it is removed from service, and a column containing fresh carbon is added at the discharge end of the series. An alternative approach is the moving bed column (73). In this design the adsorption zone is contained within a single column by passing liquid upward while continuously or intermittently withdrawing spent carbon at the bottom and adding fresh carbon at the top.

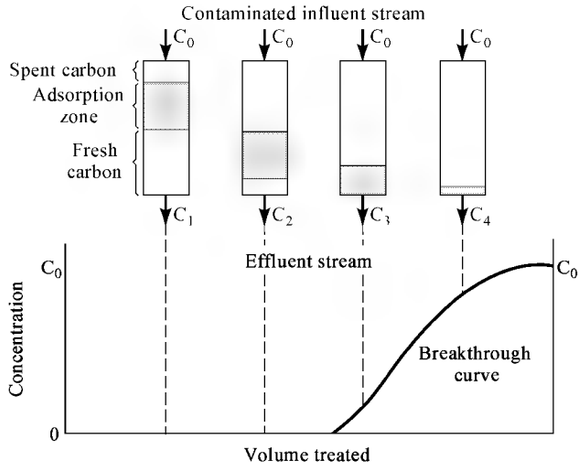

Fig. 4. Adsorption zone and breakthrough curve for fixed bed of granular or shaped activated carbon.

The total activated carbon consumption for liquid-phase applications in the United States in 1987 was estimated to be about 76,700 t, which accounted for nearly 80% of the total activated carbon use. The consumption by application is summarized in Table 5 (74).

Table 5. Liquid-Phase Activated Carbon Consumption[a], 10^3 t

	Granular-shaped	Powdered	Total
potable water	4.5	13.6	18.1
wastewater			
industrial	6.4	6.6	13.0
municipal	0.9	2.0	2.9
sweetener decolorization	6.8	9.1	15.9
chemical processing and misc.	4.1	2.3	6.4
food, beverage, and oils	0.9	3.9	4.8
pharmaceuticals	2.0	2.3	4.3
mining	1.6	2.5	4.1
groundwater	0.9	2.3	3.2
household uses	1.4	0.9	2.3
dry cleaning	0.7	0.4	1.1
electroplating	0.2	0.4	0.6
Total	*30.4*	*46.3*	*76.7*

[a] In the United States, 1987.

Potable Water Treatment. Treatment of drinking water accounts for about 24% of the total activated carbon used in liquid-phase applications (74). Rivers, lakes, and groundwater from wells, the most common drinking water sources, are often contaminated with bacteria, viruses, natural vegetation decay products, halogenated materials, and volatile organic compounds. Normal water disinfection and filtration treatment steps remove or destroy the bulk of these materials (75). However, treatment by activated carbon is an important additional step in many plants to remove toxic and other organic materials (76–78) for safety and palatability.

Groundwater Remediation. Concern over contaminated groundwater sources increased in the 1980s, and in 1984 an Office of Groundwater Protection was created by the EPA (74). This led to an increase in activated carbon consumption in 1987 for groundwater treatment to about 4% of the total liquid-phase usage, and further growth is expected in the 1990s. There are two ways to apply carbon in groundwater cleanup. One is the conventional method of applying powdered, granular, or shaped carbon to adsorb contaminants directly from the water. The other method utilizes air stripping to transfer the volatile compounds from water to air. The compounds are then recovered by passing the contaminated air through a bed of carbon (79,80).

Industrial and Municipal Wastewater Treatment. Wastewater treatment consumes about 21% of the total U.S. liquid-phase activated carbon (74), and governmental regulations are expected to increase demand over the next several years. Wastewater may contain suspended solids, hazardous microorganisms, and toxic organic and inorganic contaminants that must be removed or destroyed before discharge to the environment. In tertiary treatment systems, powdered, granular, or shaped carbon can be used to remove residual toxic and other organic compounds after the primary filtration and secondary biological treatment (81). Powdered carbon is also used in the PACT process by direct addition of the carbon to the secondary biological treatment step (47) (see WATER, INDUSTRIAL WATER TREATMENT; WATER, MUNICIPAL WATER TREATMENT).

Sweetener Decolorization. About 21% of the liquid-phase activated carbon is used for purification of sugar (qv) and corn syrup (74). White sucrose sugar is made from raw juice squeezed from sugar cane or sugar beets. The clarified liquor is decolorized using activated carbon, or ion-exchange resins (82). High fructose corn sweeteners (HFCS) are produced by hydrolysis of corn starch and are then treated with activated carbon to remove undesirable taste and odor compounds and to improve storage life. The demand for HFCS rose sharply in the 1980s primarily because of the switch by soft drink producers away from sucrose (83).

Chemical Processing. Activated carbon consumption in a variety of chemical processing applications is about 8% of the total (74). The activated carbon removes impurities to achieve high quality. For example, organic contaminants are removed from solution in the production of alum, soda ash, and potassium hydroxide (82). Other applications include the manufacture of dyestuffs, glycols, amines, organic acids, urea, hydrochloric acid, and phosphoric acid (83).

Food, Beverage, and Cooking Oil. Approximately 6% of the liquid-phase activated carbon is used in food, beverage, and cooking oil production (74). Before being incorporated into edible products, vegetable oils and animal fats are refined to remove particulates, inorganics, and organic contaminants. Activated carbon is one of several agents used in food purification processes. In the production of alcoholic beverages, activated carbon removes haze-causing compounds from beer, taste and odor from vodka, and fusel oil from whiskey (82). The feed water for soft drink production is often treated with carbon to capture undesirable taste and odor compounds and to remove free chlorine remaining from disinfection treatment. Caffeine is removed from coffee beans by extraction with organic solvents, water, or supercritical carbon dioxide prior to roasting. Activated carbon is used to remove the caffeine from the recovered solvents (83).

Pharmaceuticals. Pharmaceuticals account for 6% of the liquid-phase activated carbon consumption (74). Many antibiotics, vitamins, and steroids are isolated from fermentation broths by adsorption onto carbon followed by solvent extraction and distillation (82). Other uses in pharmaceutical production include process water purification and removal of impurities from intravenous solutions prior to packaging (83).

Mining. The mining industry accounts for only 4% of liquid-phase activated carbon use, but this figure may grow as low-grade ores become more common (74). Gold, for example, is recovered on activated carbon as a cyanide complex in the carbon-in-pulp extraction process (82). Activated carbon serves as a catalyst in the detoxification of cyanides contained in wastewater from cyanide stripping operations (73). Problems caused by excess flotation agent concentrations in flotation baths are commonly cured by adding powdered activated carbon (82).

Miscellaneous Uses. Several relatively low volume activated carbon uses comprise the remaining 6% of liquid-phase carbon consumption (74). Small carbon filters are used in households for purification of tap water. Oils, dyes, and other organics are adsorbed on activated carbon in dry cleaning recovery and recycling systems. Electroplating solutions are treated with carbon to remove organics that can produce imperfections when the thin metal layer is deposited on the substrate (82). Medical applications include removal of toxins from the blood of patients with artificial kidneys (83) and oral ingestion into the stomach to recover poisons or toxic materials (82,84). Activated carbon also is used as a support for metal catalysts in low volume production of high value specialty products such as pharmaceuticals, fragrance chemicals, and pesticides (85).

Gas-Phase Applications

Gas-phase applications of activated carbon include separation, gas storage, and catalysis. Although only 20% of activated carbon production is used for gas-phase applications, these products are generally more expensive than liquid-phase carbons and account for about 40% of the total dollar value of shipments. Most of the activated carbon used in gas-phase applications is granular or shaped. Activated carbon use by application is shown in Table 6 (86). Separation processes comprise the main gas-phase applications of activated carbon. These usually exploit the differences in the adsorptive behavior of gases and vapors on activated carbon on the basis of molecular weight and size. For example, organic molecules with a molecular weight greater than about 40 are readily removed from air by activated carbon (see ADSORPTION, GAS SEPARATION).

Table 6. Gas-Phase Activated Carbon Uses[a]

Application	Consumption, 10^3 t

solvent recovery	4.5
automotive gasoline recovery	4.1
industrial off-gas control	3.2
catalysis	2.7
pressure swing separation	1.1
air conditioning	0.5
gas mask	0.5
cigarette filters	0.5
nuclear	0.3
Total	*17.4*

[a] In the United States, 1987.

Solvent Recovery. Most of the activated carbon used in gas-phase applications is employed to prevent the release of volatile organic compounds into the atmosphere. Much of this use has been in response to environmental regulations, but recovery and recycling of solvents from a range of industrial processes such as printing, coating, and extrusion of fibers also provides substantial economic benefits.

The structure of activated carbons used for solvent recovery has been predominantly microporous. Micropores provide the strong adsorption forces needed to capture small vapor molecules such as acetone at low concentrations in process air (87). In recent years, however, more mesoporous carbons, specifically made for solvent recovery, have become available and are giving good service, especially for the adsorption of heavier vapors such as cumene- and cyclohexanone that are difficult to remove from micropores during regeneration (87). Regeneration of the carbon is performed on a cyclic basis by purging it with steam or heated nitrogen.

Gasoline Emission Control. A principal application of activated carbon is in the capture of gasoline vapors that escape from vents in automotive fuel systems (88). Under EPA regulations, all U.S. motor vehicles produced since the early 1970s have been equipped with evaporative emission control systems. Most other auto producing countries now have similar controls. Fuel vapors vented when the fuel tank or carburetor are heated are captured in a canister containing 0.5 to 2 L of activated carbon. Regeneration of the carbon is then accomplished by using intake manifold vacuum to draw air through the canister. The air carries desorbed vapor into the engine where it is burned during normal operation. Activated carbon systems have also been proposed for capturing vapors emitted during vehicle refueling, and activated carbon is used at many gasoline terminals to capture vapor displaced when tank trucks are filled (89). Typically, the adsorption vessels contain around 15 m^3 of activated carbon and are regenerated by application of a vacuum. The vapor that is pumped off is recovered in an absorber by contact with liquid gasoline. Similar equipment is used in the transfer of fuel from barges (90). The type of carbon pore structure required for these applications is substantially different from that used in solvent recovery. Because the regeneration conditions are very mild, only the weaker adsorption forces can be overcome, and therefore the most effective pores are in the mesopore size range (91). A large adsorption capacity in these pores is possible because vapor concentrations are high, typically 10–60%.

Adsorption of Radionuclides. Other applications that depend on physical adsorption include the control of krypton and xenon radionuclides from nuclear power plants (92). The gases are not captured entirely, but their passage is delayed long enough to allow radioactive decay of the short-lived species. Highly microporous coconut-based activated carbon is used for this service.

Control by Chemical Reaction. Pick-up of gases to prevent emissions can also depend on the chemical properties of activated carbon or of impregnants. Emergency protection against radioiodine emissions from nuclear power reactors is provided by isotope exchange over activated carbon impregnated with potassium iodide (93). Oxidation reactions catalyzed by the carbon surface are the basis for several emission control strategies. Sulfur dioxide can be removed from industrial off-gases and power plant flue gas because it is oxidized to sulfur trioxide, which reacts with water to form nonvolatile sulfuric acid (94,95). Hydrogen sulfide can be removed from such sources as Claus plant tail gas because it is converted to sulfur in the presence of oxygen (96). Nitric oxide can be removed from flue gas because it is oxidized to nitrogen dioxide. Ammonia is added and reacts catalytically on the carbon surface with the nitrogen dioxide to form nitrogen (97).

Protection Against Atmospheric Contaminants. Activated carbon is widely used to filter breathing air to protect against a variety of toxic or noxious vapors, including war gases, industrial chemicals, solvents, and odorous compounds. Activated carbons for this purpose are highly microporous and thus maximize the adsorption forces that hold adsorbate molecules on the surface. Although activated carbon can give protection against most organic gases, it is especially effective against high molecular weight vapors, including chemical warfare agents such as mustard gas or the nerve agents that are toxic at parts per million concentrations. The activated carbon is employed in individual canisters or pads, as in gas masks, or in large filters in forced air ventilation systems. In airconditioning systems, adsorption on activated carbon can be used to control the buildup of odors or toxic gases like radon in recirculated air (98).

Inorganic vapors are usually not strongly adsorbed on activated carbon by physical forces, but protection against many toxic agents is achieved by using activated carbon impregnated with specific reactants or decomposition catalysts. For example, a combination of chromium and copper impregnants is used against hydrogen cyanide, cyanogen, and cyanogen chloride, whereas silver assists in the removal of arsine. All of these are potential chemical warfare agents; the Whetlerite carbon, which was developed in the early 1940s and is still used in military protective filters, contains these impregnants (99). Recent work has shown that chromium, which loses effectiveness with age and is itself toxic, can be replaced with a combination of molybdenum and triethylenediamine (100). Oxides of iron and zinc on activated carbon have been used in cigarette filters to absorb hydrogen cyanide and hydrogen sulfide (101). Mercury vapor in air can be removed by activated carbon impregnated with sulfur (102). Activated carbon impregnated with sodium or potassium hydroxide has long been used to control odors of hydrogen sulfide and organic mercaptans in sewage treatment plants (103). Alkali-impregnated carbon is also effective against sulfur dioxide, hydrogen sulfide, and chlorine at low concentrations. Such impregnated carbon is used extensively to protect sensitive electronic equipment against corrosion by these gases in industrial environments (104).

Process Stream Separations. Differences in adsorptivity between gases provides a means for separating components in industrial process gas streams. Activated carbon in fixed beds has been used to separate aromatic compounds from lighter vapors in petroleum refining process streams (105) and to recover gasoline components from natural and manufactured gas (106,107).

Molecular sieve activated carbons are specially made with restricted openings leading to micropores. These adsorbents are finding increasing use in separations utilizing pressure swing adsorption, in which adsorption is enhanced by operation at high pressure and desorption occurs upon depressurization (108). Larger molecules are restricted from entrance into the pores of these carbons and, therefore, are not retained as strongly as smaller molecules. The target product can be either the adsorbed or unadsorbed gases. Examples include separation of oxygen from air and recovery of methane from inorganic gases in biogas production. Hydrogen can be removed from gases produced in the catalytic cracking of gasoline, and carbon monoxide can be separated from fuel gases. Use of pressure swing techniques for gas separation is an area of growing interest in engineering research.

The Hypersorption process developed in the late 1940s used a bed of activated carbon moving countercurrent to gas flow to separate light hydrocarbons from each other and from hydrogen in refinery operations. The application is of interest because of its scale, treating up to 20,000 m^3 h of gas, but the plants were shut down within a few years, probably because of problems related to attrition of the rapidly circulating activated carbon (109). It should be noted, however, that in recent years moving-bed and fluid-bed adsorption equipment using activated carbon has been successfully employed for solvent recovery (110).

Gas Storage. Adsorption forces acting on gas molecules held in micropores significantly densify the adsorbed material. As a result, activated carbon has long been considered a medium for lowering the pressure required to store weakly adsorbed compressed gases (111). Recent work with modern high capacity carbons has been directed toward fueling passenger cars with natural gas, but storage volume targets have not yet been attained (112). Natural gas storage on activated carbon is now used commercially in portable welding cylinders (113). These can be refilled easily at about 2000 kPa and hold as much gas as a conventional cylinder pressurized to 6000 kPa (59 atm).

Catalysis. Catalytic properties of the activated carbon surface are useful in both inorganic and organic synthesis. For example, the fumigant sulfuryl fluoride is made by reaction of sulfur dioxide with hydrogen fluoride and fluorine over activated carbon (114). Activated carbon also catalyzes the addition of halogens across a carbon–carbon double bond in the production of a variety of organic halides (85) and is used in the production of phosgene

from carbon monoxide and chlorine (115,116).

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CARBON BLACK

Carbon black is a generic term for an important family of products used principally for the reinforcement of rubber, as a black pigment, and for its electrically conductive properties. It is a fluffy powder of extreme fineness and high surface area, composed essentially of elemental carbon. Plants for the manufacture of carbon black are strategically located worldwide in order to supply the rubber tire industry, which consumes 70% of production. About 20% is used for other rubber products and 10% is used for special nonrubber applications. World capacity in 1988 was estimated at over six million metric tons; U.S. capacity was almost 1.6 million metric tons. Carbon black was ranked 38 in 1989 among the 50 largest volume industrial chemicals produced in the United States. Six U.S. manufacturers (1) were operating 22 plants in 1990. Many of these are located in the south and southwest. Over 35 grades, listed in ASTM 1765-87 (2), are used by the rubber industry, and one manufacturer supplies an additional 45 grades for special pigment applications.

Carbon blacks differ from other forms of bulk carbon such as diamond, graphite, cokes, and charcoal in that they are particulate, composed of aggregates having complex configurations, quasigraphitic in structure, and of colloidal dimensions. They differ from other bulk carbons in having their origin in the vapor phase through the thermal decomposition and the partial combustion of hydrocarbons. Carbon black is a product of a process incorporating the latest engineering technology and process controls. Its purity differentiates it from soots that are impure by-products from the combustion of coal and oils and from the use of diesel fuels. Carbon blacks are essentially free of the inorganic contaminants and extractable organic residues characteristic of most forms of soot.

A number of processes have been used to produce carbon black including the oil-furnace, impingement (channel), lampblack, and the thermal decomposition of natural gas and acetylene (3). These processes produce different grades of carbon and are referred to by the process by which they are made, eg, oil-furnace black, lampblack, thermal black, acetylene black, and channel-type impingement black. A small amount of by-product carbon from the manufacture of synthesis gas from liquid hydrocarbons has found applications in electrically conductive compositions. The different grades from the various processes have certain unique characteristics, but it is now possible to produce reasonable approximations of most of these grades by the oil-furnace process. Since over 95% of the total output of carbon black is produced by the oil-furnace process, this article emphasizes this process.

History of Carbon Black Manufacture

The use of carbon black as a pigment dates back to prehistoric times. Cave wall dwellings and objects from ancient Egypt were decorated with paints and lacquers containing carbon black. The oldest process practiced in China about 3000 BC consisted of the partial combustion of vegetable oils in small lamps with ceramic covers. The smoke impinged on the covers from which the adhering carbon black was carefully removed. Another old process is the lampblack process, which is the ancestor of all modern carbon blacks. Until the 1870s it was the only commercial process, and because of this the world lampblack is occasionally used as a generic term for carbon black. In the lampblack process, oils are burned in open, shallow pans in a restricted air supply. The heavy, carbon-laden smoke is passed through a series of settling chambers and filters from which the flocculated carbon deposits are recovered.

Prior to 1870 it was already known that carbon black with much higher covering power and jetness could be recovered from underventilated illuminating gas flames impinging on a cold surface. These gas blacks led to the development of the channel process, the name deriving from the iron channels used for the collection of the carbon blacks from the impingement of thousands of small luminous flames burning in a restricted atmosphere of air. This process dominated the industry for over 50 years. In 1926 there were 33 producers in the United States. Because of poor carbon yields from natural gas in the range of 1–5% and severe atmospheric pollution, this process has become extinct. The last channel black plant in the United States was closed in 1976.

In the 1920s two other processes using natural gas were introduced that gave much higher yields with large decreases in atmospheric contamination. One was the cyclic thermal black process. Alternate heating and production cycles in large brick checkered chambers are used to produce a unique large particle size, essentially unaggregated-grade useful for many special rubber and plastic applications. Thermal black is produced in the United States, Canada, England, and a few other locations worldwide. The other process, based on natural gas, was the so-called gas-furnace process and is no longer used. This process was continuous and the forerunner of the oil-furnace process. It was discontinued because of the relatively low yield, high raw material cost, and limited range of products.

The first commercial oil-furnace process was put into operation in 1943 by the Phillips Petroleum Co. in Borger, Texas. The oil-furnace blacks rapidly displaced all other types used for the reinforcement of rubber and today account for practically all carbon black production. In the oil-furnace process heavy aromatic residual oils are atomized into a primary combustion flame where the excess oxygen in the primary zone burns a portion of the residual oil to maintain flame temperatures, and the remaining oil is thermally decomposed into carbon and hydrogen. Yields in this process are in the range of 35 to 50% based on the total carbon input. A broad range of product qualities can be produced.

Before World War I carbon black was almost exclusively used as a black pigment for printing inks, paints, and enamels. The singular event that changed the industry from a small specialty product manufacturer to large volume producer of a vital raw material was the discovery of rubber reinforcement in 1904 (4). The automobile and the tire industries were expanding rapidly, and there was a demand for longer wearing automobile tires. The use of carbon black as a filler for rubber fulfilled this need providing longer wearing and more durable pneumatic tires. The use of carbon black in tires remains its most important application, coupling the fortunes of the carbon black industry to that of the automotive industry.

Physical Structure of Carbon Black

Molecular and Crystallite Structure. The arrangement of carbon atoms in carbon black has been well-established by x-ray diffraction methods (5,6). The diffraction patterns show diffuse rings at the same positions as diffraction rings from pure graphite. The suggested relation to graphite is further emphasized as carbon black is heated to 3000°C. The diffuse reflections sharpen, but the pattern never achieves that of true graphite. Carbon black can have a degenerated graphitic crystallite structure. Whereas graphite has three-dimensional order, as seen in the model structures of Figure 1, carbon black has two-dimensional order. The x-ray data indicate that carbon black consists of well-developed graphite platelets stacked roughly parallel to one another but random in orientation with respect to adjacent layers. As shown in Figure 1 the carbon atoms in the graphite structure form large sheets of condensed aromatic ring systems with an interatomic spacing of 0.142 nm, comparable to the aromatic carbon separation distance of 0.139 nm in benzene. The large graphite interplanar distance of 0.335 nm results in a specific gravity of 2.26. In carbon black the interplanar distance is still larger, in the range of 0.350–0.365 nm, as a consequence of the random planar orientations or so-called turbostratic arrangement. The specific gravities of commercial carbon blacks are 1.76–1.90 depending on the grade. X-ray diffraction data provide estimates of crystallite size. L_a is the average layer plane diameter and L_c is the average crystallite thickness. For a typical carbon black L_a is 1.7 nm and L_c is 1.5 nm, which corresponds to an average of four layer planes per crystallite containing 375 carbon atoms. A particle of a 100 m^2 g carbon black contains over 4000 crystallites. It was originally suggested that these discrete crystallites were in random orientation within the particle. This view was later abandoned when electron microscopy of graphitized and oxidized carbon blacks indicated more of a concentric layer plane arrangement. This structure has been confirmed by the use of high resolution phase-contrast electron microscopy that made possible the direct imaging of graphitic layer planes in carbon black (7). Figure 2 shows a phase-contrast electron micrograph of carbon black at high resolution that displays the marked concentric arrangement of the layer planes at the surface and around what appear to be growth

centers.

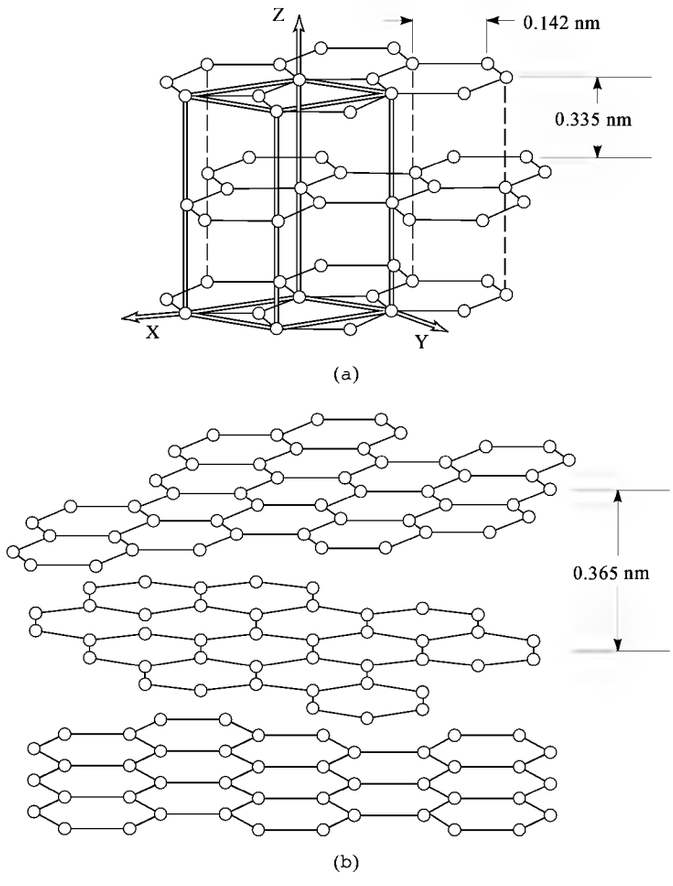

Fig. 1. Atomic structural models of (**a**), graphite, and (**b**), carbon black.

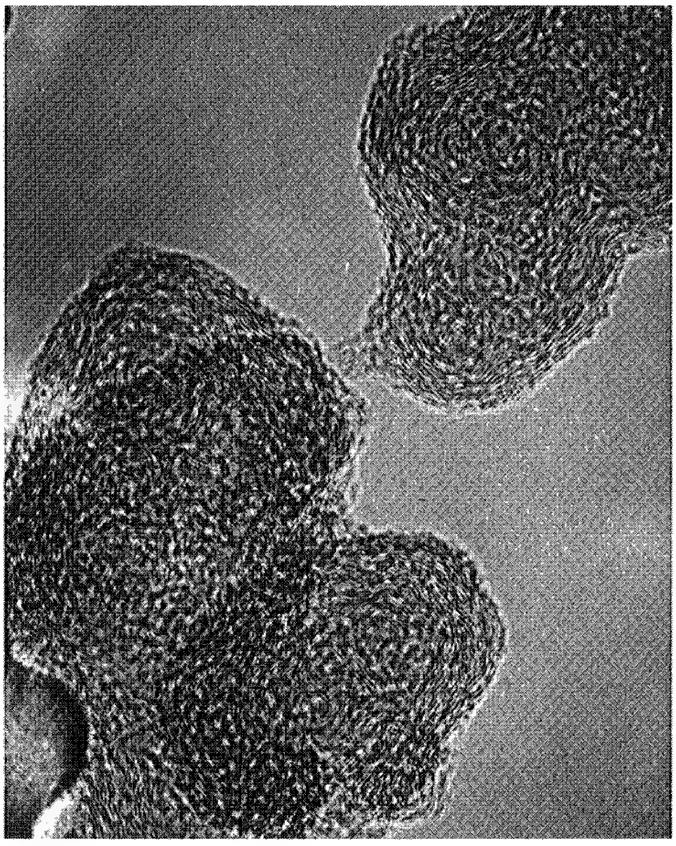

Fig. 2. High resolution (3,000,000 ×) electron micrograph of H-300-grade carbon black.

Courtesy of W. M. Hess.

The word particle has become so widely used in the technical rubber and carbon black literature that it is convenient to retain the term when in fact nodule is meant. The layer planes are curved, distorted, and of varying size. They also intersect and interconnect one particle or nodule with its neighbors. This type of structure has been termed paracrystalline. It is obvious that individual particles do not exist in carbon blacks, with the exception of thermal

blacks, and that the functional unit is an aggregate of nodules that probably existed as smaller particles at some early stage of the carbon formation process. The functional unit in well-dispersed systems is called an aggregate.

Morphology. In describing carbon black, three terms are used to describe structures of increasing scale and complexity:

Particles (nodules) are the primary structure element. They are roughly spherical elements that are joined in the aggregate structures.

Aggregates are the primary dispersable elements of carbon black in all but thermal blacks. The particles in an aggregate are connected and have grown together.

Agglomerates are undispersed clusters of aggregates held together by van der Waals forces or by binders. The term structure is used to describe both the extent and the complexity with which the particles are interconnected in aggregates. Primary measures of structure focus on the internal space within the aggregate.

Size and shape of the aggregates in composite systems are the principal features that determine the performance of carbon black as a reinforcing agent and as a pigment (8). Figure 3 shows an electron micrograph of a reinforcing tread black. There is an enormous range in aggregate size. The aggregate size distribution curve for N220 shown in Figure 4 is log-normal, and the range of D_e, equivalent diameters of the projected areas of the aggregates is about tenfold. Within each aggregate the nodules, or particles, appear to be about the same size. The size of the aggregates is directly related to the size of the particles. The shapes of the aggregates have infinite variety from tight grapelike clusters to open dendritic or branched arrangements to fibrous configurations.

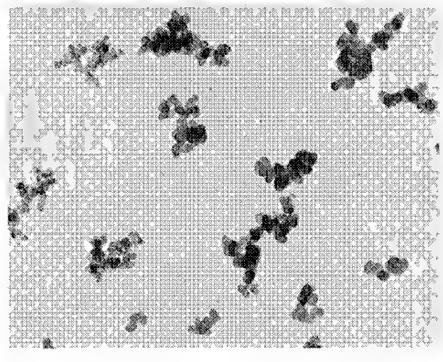

Fig. 3. Electron micrograph of reinforcing-grade of N399 tread black (100,000×).

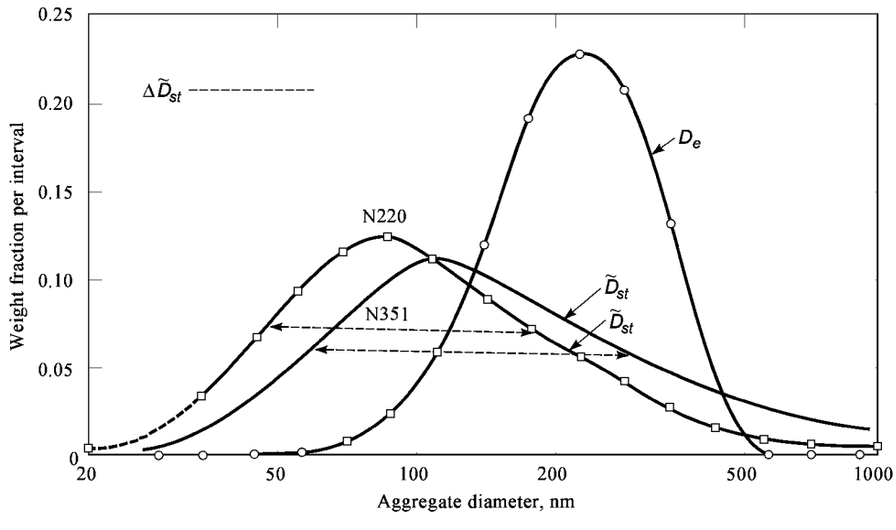

Fig. 4. Aggregate size distributions by electron microscope image analysis (D_e) and centrifugal ($D\sim_{St}$) sedimentations for N220 and N351 carbon blacks (8).

A useful method for determining relative aggregate sizes and distributions is by centrifugal sedimentation. From the sedimentation rates of the aggregates the Stokes diameter is derived. A convenient instrument for these measurements is the Joyce Loebl disk photosedimentometer (9). Large aggregates sediment at a faster rate than smaller ones. The sedimentation rate is also influenced by the bulkiness of the aggregates. At constant volume or mass, a bulky aggregate sediments more slowly than a compact aggregate because of frictional drag. Figure 4 (8) shows a comparison of a Stokes diameter distribution $D\sim_{St}$ and equivalent diameter distribution D_e from electron microscopy for N220. In this example the modal $D\sim_{St}$ value is about one-third of the modal D_e value.

Table 1 lists average $D\sim_{St}$ values from a number of literature sources. This table also lists d_{nm} values for the aggregates calculated from their estimated volumes. In this case there is reasonable agreement between the two diameters. Aggregate size distributions from centrifugal sedimentation analysis are very useful for assessing the differences in this characteristic within a given grade or at constant surface area. It has been shown that the hysteresis of rubber vulcanizates can be reduced by broadening the aggregate size distribution curve without any significant loss in abrasion resistance (11,12). As shown in Figure 4 this broadening is usually expressed as ΔD_{50}, the width at 50% of the modal value. $D\sim_{St}$ values have been related to the dynamic and mechanical performance of rubber-grade carbon blacks. Hysteresis decreases and abrasion loss increases with increasing values of $D\sim_{St}$ (13).

Table 1. Carbon Black Morphology[a]

ASTM designation	Particle size, d_{nm}[b], nm	Aggregate size, d_{nm}[b], nm	$D\sim_{St}$[c], nm	Surface area, m^2/g
N110	27	93	76–111	143

N220	32	103	95–117	117
N234	31	109	74–97	120
N326	41	108	98	94
N330	46	146	116–145	80
N339	39	122	96–125	96
N351	50	159	127	75
N375	36	106	91	105
N550	93	240	220–242	41
N660	109	252	227–283	34
N774	124	265	261	30
N990	403	593	436	9

[a] Ref. 10. Particle size, aggregate size, and surface area are by em.

[b] d_{wm} weight mean diameter $\frac{nd^4}{nd^3}$.

[c] Stokes diameter by centrifugal sedimentation from various sources.

The tinting strength of rubber-grade carbon blacks shows a linear relationship with $D\sim_{St}$ shown in Figure 5. Since performance characteristics are known to depend on aggregate volume, surface area, and bulkiness, it appears that the $D\sim_{St}$ values combine the effects of all these factors. As such, it is a valuable addition to carbon black characterization methodology.

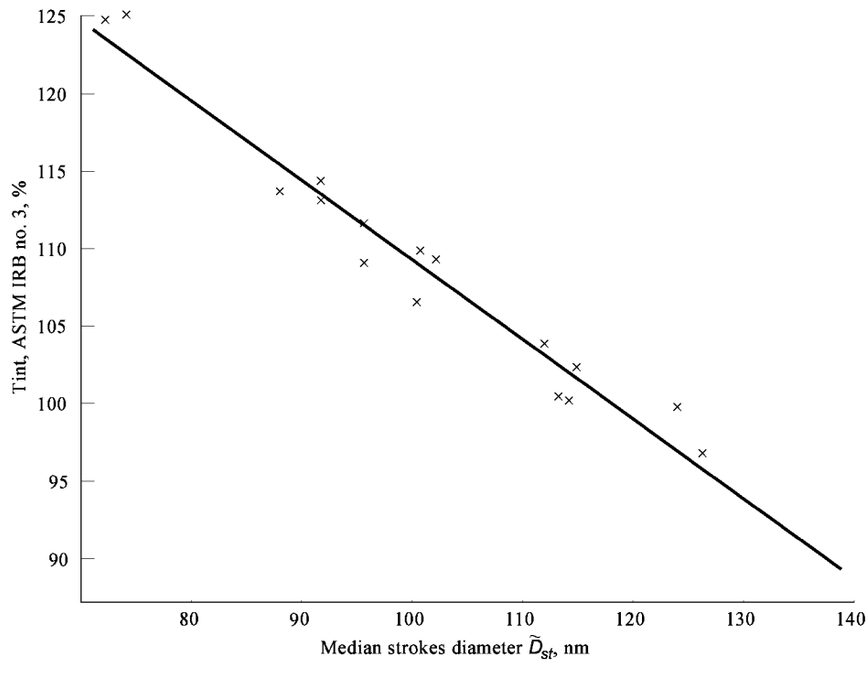

Fig. 5. Tinting strength versus median Stokes diameters for a range of reinforcing tread blacks.

Aggregate Morphology and Structure. The term structure is widely used in the carbon black and rubber industries. It was originally introduced in 1944 (14) to describe a chaining tendency of the carbon black particles. It is now used to describe the relative void volume characteristics of grades of black of the same surface area. Structure comparisons of grades with different surface areas cannot be made. It is now known that the properties associated with structure are associated principally with the bulkiness of individual aggregates. Aggregates of the same volume, surface area, and number of nodules have high structure in the open bulky and filamentous arrangement and a low structure in a more clustered compact arrangement.

High structure blacks in unvulcanized rubber give higher Mooney viscosities, lower die swell, faster extrusion rates, and better and more rapid dispersion after incorporation. In vulcanized rubber higher modulus is obtained. High structure blacks give lower bulk densities and high vehicle demand in paint systems.

Structure is usually measured by a void volume test such as the absorption of dibutyl phthalate (DBPA) (15), or by bulk density measurements of the carbon black under compression. In order to eliminate the effects of pelletizing conditions the DBPA test has been modified to use a sample that has been precompressed at a pressure of 165 MPa (24,000 psi) and then broken up four successive times (24M4) (16). This procedure causes some aggregate breakdown and is claimed to more closely approximate the actual breakdown that occurs during rubber mixing.

Aggregate Breakdown. Aggregate size analysis by the electron microscope and centrifuge methods are performed on predispersed samples of carbon black. High shear energy, usually ultrasonic, and enough time are employed in these sample preparations to break down microagglomerates to their ultimate aggregates for measurement. When mixed into elastomers under high shear conditions the aggregates themselves undergo fracture forming smaller aggregates that become the actual functional units (17–19). The extent of breakdown depends on shearing stress, energy input, and the grade of carbon black. Elastomer mixes were studied using the techniques of ultramicrotome and automated image analysis. Ultrasonic dispersions of carbon gel preparations from elastomer mixes have also been used in breakdown studies. A high DBPA reinforcing tread grade (N347) exhibited a significant reduction in aggregate length in a BR OEP tread formulation, whereas a low DBPA grade (N326) showed no measurable change. The extent of aggregate length reduction was 30 to 40% for the normal and high DBPA grades (20).

The effect of elastomer viscosity on aggregate breakdown has been shown (19). A high DBPA grade (N339) was well-mixed with a 52 and a 100 Mooney viscosity OE-SBR. A 43% reduction in aggregate volume was reported for the 52 Mooney rubber and a 53% reduction for 100 Mooney rubber. High resolution electron micrographs show actual fracture locations at the ends of aggregates. The extent of fracture from aggregate length and volume breakdown is consistent with one average fracture per aggregate for the high DBPA grades.

Chemical Composition

Oil-furnace blacks used by the rubber industry contain over 97% elemental carbon. Thermal and acetylene black consist of over 99% carbon. The ultimate analysis of rubber-grade blacks is shown in Table 2. The elements other than carbon in furnace black are hydrogen, oxygen, and sulfur, and there are mineral oxides and salts and traces of adsorbed hydrocarbons. The oxygen content is located on the surface of the aggregates as C_xO_y complexes. The

hydrogen and sulfur are distributed on the surface and the interior of the aggregates. Some special blacks used for pigment purposes contain larger quantities of oxygen than normal furnace blacks. These blacks are made by oxidation in a separate process step using nitric acid, ozone, air, and other oxidizing agents. They may contain from 2 to 6% oxygen. Oxidation improves dispersion and flow characteristics in pigment vehicle systems such as lithographic inks, paints, and enamels. In rubber-grade blacks surface oxidation reduces pH and changes the kinetics of vulcanization, making the rubber compounds less scorchy and slower curing.

Table 2. Chemical Composition of Carbon Blacks, %

Type	Carbon	Hydrogen	Oxygen	Sulfur	Ash	Volatile
rubber-grade furnace	97.3–99.3	0.20–0.40	0.20–1.20	0.20–1.20	0.10–1.00	0.60–1.50
medium thermal	99.4	0.30–0.50	0.00–0.12	0.00–0.25	0.20–0.38	
acetylene	99.8	0.05–0.10	0.10–0.15	0.02–0.05	0.00	<0.40

A convenient method for assessing the extent of surface oxidation is the measurement of volatile content. This standard method measures the weight loss of the evolved gases on heating up to 950°C in an inert atmosphere. The composition of these gases consists of three principal components: hydrogen, carbon monoxide, and carbon dioxide. The volatile content of normal furnace blacks is under 1.5%, and the volatile content of oxidized special grades is 2.0 to 9.5%.

The origin of the volatile gases is the functional groups attached to the carbon black layer planes. These groups are carbon-bound hydrogen, phenols, hydroquinones, quinones, neutral groups with one oxygen, carboxylic acids, lactones, and neutral groups containing two oxygens (21). Hydrogen is the most dominant of these groups. The oxygen content is present mainly as weakly acidic phenolic groups located at the surface of the aggregates. Figure 6 shows an idealized graphite surface layer plane with the various functional groups located at the periphery of the plane.

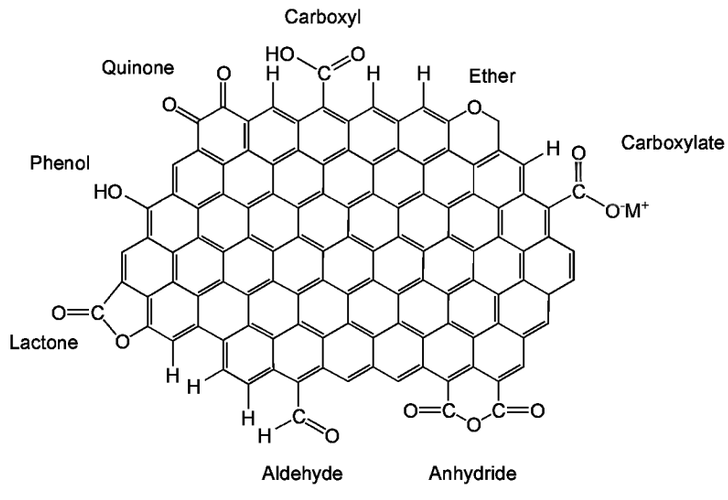

Fig. 6. Aromatic layer plane with functional side groups.

In addition to combined hydrogen and oxygen, carbon blacks may contain as much as 1.2% combined sulfur resulting from the sulfur content of the aromatic feedstock that contains thiophenes, mercaptans, and sulfides. The combined sulfur appears to be inert and does not contribute to sulfur cross-linking during the vulcanization of rubber compounds.

The ash content of furnace blacks is normally a few tenths of a percent but in some products may be as high as one percent. The chief sources of ash are the water used to quench the hot black from the reactors during manufacture and for wet pelletizing the black. The hardness of the water, and the amount used determines the ash content of the products. The ash consists principally of the salts and oxides of calcium, magnesium, and sodium and accounts for the basic pH (8–10) commonly found in furnace blacks. In some products potassium, in small amounts, is present in the ash content. Potassium salts are used in most carbon black manufacture to control structure and rubber vulcanizate modulus (22). The basic mineral salts and oxides have a slight accelerating effect on the vulcanization reaction in rubber.

Carbon Black Formation Mechanisms

The formation of carbon black in a candle flame was the subject of a series of lectures in the 1860s by Michael Faraday at the Royal Institution in London (23). Faraday described the nature of the diffusion flame, the products of combustion, the decomposition of the paraffin wax to form hydrogen and carbon, the luminosity of the flame because of incandescent carbon particles, and the destructive oxidation of the carbon by the air surrounding the flame. Since Faraday's time, many theories have been proposed to account for carbon formation in a diffusion flame, but controversy still exists regarding the mechanism (24).

Mechanisms of formation must account for the unique morphology and microstructure of carbon black. These features include the presence of nodules, or particles, multiple growth centers within some nodules, the fusion of nodules into large aggregates, and the paracrystalline or concentric layer plane structure of the aggregates. One mechanism of formation involves the decomposition of the aromatic hydrocarbon fuel in a diffusion flame to hydrogen and carbon radicals, and carbon–hydrogen radical fragments. These combine into larger aromatic layer plane units until they are no longer stable and condense out of the vapor phase to form nuclei, or growth centers. Further carbon deposition forms carbon particles that are the precursors of the nodules. The carbon particles collide and coalesce while undergoing further deposition of carbon layer planes and their surface, forming the nodules and aggregates with their characteristic onion microstructure as seen in the micrographs (25). The various steps in the sequence are not well understood. There is particular disagreement regarding the nucleation and particle formation steps preceding the formation of nodules. One suggestion is that the particles go through a fairly sticky stage as they collide and coalesce to form the aggregates. Another suggestion is that the layer planes formed in the vapor phase condense out to form solid multiple layer plane nuclei. Carbon deposition on the nuclei results in particles and eventually nodules and aggregates. The remarkable and industrially important influence of ionic species such as K^+ and Ca^{2+} on the morphology of the aggregates and their surface area during the carbon black formation process is a strong indication that ionic mechanisms may be active in the nucleation and aggregate formation steps (22). There are several reviews of carbon formation mechanisms (26,27).

Manufacture

THE OIL-FURNACE PROCESS

The oil-furnace process, based on the partial combustion of liquid aromatic residual hydrocarbons, was first introduced in the United States at the end of World War II. It rapidly displaced the then dominant channel (impingement) and gas-furnace processes because it gave improved yields and better product qualities. It was also independent of the geographical source of raw materials, a limitation on the channel process and other processes dependent on natural gas, making possible the worldwide location of manufacturing closer to the tire customers. Environmentally it favored elimination of particulate air pollution and was more versatile than all other competing processes.

A simplified flow diagram of a modern furnace black production line is shown in Figure 7 (28). The principal pieces of equipment are the air blower, process air and oil preheaters, reactors, quench tower, bag filter, pelletizer, and rotary dryer. The basic process consists of atomizing the feedstock into the combustion zone of the reactor where the combustion of natural gas and preheated excess air create a high temperature environment of 1200 to 1900°C that almost instantly vaporizes the feedstock and decomposes most of it to carbon black and hydrogen. The remaining feedstock reacts with the excess oxygen in the primary combustion stream to maintain the reaction temperature for carbon formation. In some reactors a number of feedstock streams are atomized radially into the high velocity combustion gases. The reaction products must be quenched rapidly with water sprays to lower the temperature to prevent loss of the carbon black product through reaction with carbon dioxide and water, products of the combustion reactions. The hot, heavy carbon black smoke from the reactors enters the air preheater where thermal energy is transferred to preheat the primary combustion air. From the air preheater the lower temperature combustion products are given a secondary quench for a further lowering of temperature in a tower from which they enter the bag filter that separates the fluffy carbon black product from the tail gases. Since the tail gases are composed mainly of water, nitrogen, carbon monoxide, carbon dioxide, and hydrogen, they have heating value as a fuel to supplement the natural gas used to preheat feedstock and for heating the pellet dryers. Unused tail gas is frequently flared prior to venting to the atmosphere after removal of particulate matter. The fluffy carbon black from the bag filter is mechanically agitated to increase its bulk density and is then conveyed to the wet pelletizers where water is added to transform the product into wet granules. Dry pelletization in rotating drums is practiced for some special applications. The wet pellets are then dried in a rotary dryer after which finished product goes to storage tanks for shipping in bulk or in bags.

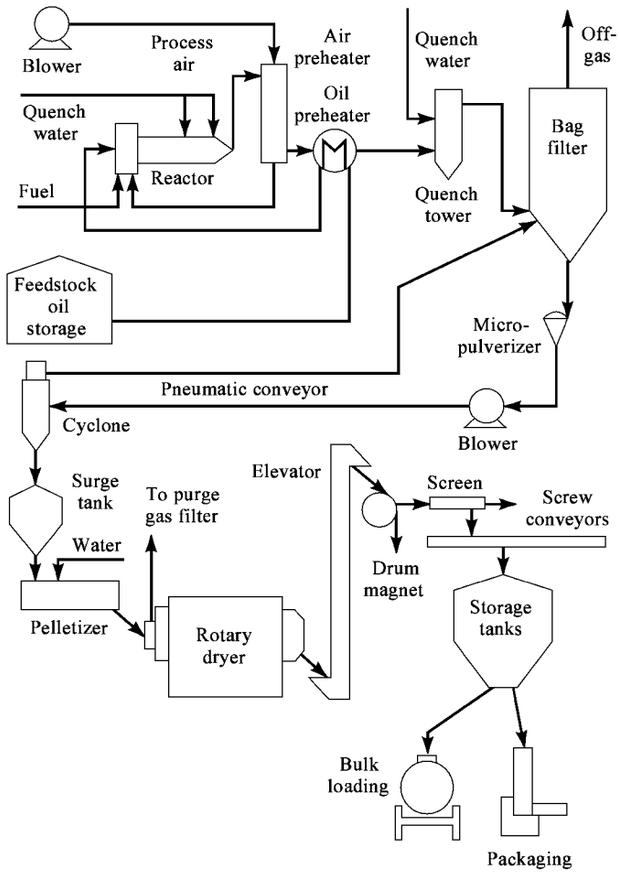

Fig. 7. Flow diagram of oil-furnace black process.

Feedstocks. Feedstocks are viscous aromatic hydrocarbons consisting of branched polynuclear aromatics with smaller quantities of paraffins and unsaturates. Preferred feedstocks are high in aromaticity, free of coke and other gritty materials, and contain low concentrations of asphaltenes, sulfur, and alkali metals. Other limitations are the quantities available on a long-term basis, uniformity, ease of transportation, and cost. The ability to handle such oils in tanks, pumps, transfer lines, and spray nozzles are also primary requirements.

The principal sources of feedstocks in the United States are the decant oils from petroleum refining operations. These are clarified heavy distillates from the catalytic cracking of gas oils. About 95% of U.S. feedstock use is decant oil. Another source of feedstock is ethylene process tars obtained as the heavy byproducts from the production of ethylene by steam cracking of alkanes, naphthas, and gas oils. There is a wide use of these feedstocks in European production. European and Asian operations also use significant quantities of coal tars, creosote oils, and anthracene oils, the distillates from the high temperature coking of coal. European feedstock sources are 50% decant oils and 50% ethylene tars and creosote oils.

Aromaticity is the most important property of a carbon black feedstock. It is generally measured by the Bureau of Mines Correlation Index (BMCI) and is an indication of the carbon-to-hydrogen ratio. The sulfur content is limited to reduce corrosion, loss of yield, and sulfur in the product. It may be limited in certain locations for environmental reasons. The boiling range must be low enough so that it will be completely volatilized under furnace time–temperature conditions. Alkane insolubles or asphaltenes must be kept below critical levels in order to maintain product quality. Excessive asphaltene content results in a loss of reinforcement and poor treadwear in tire applications.

The pricing of carbon black feedstocks depends on their alternate market as residual fuel oil, especially that of high sulfur No. 6 fuel oil. The actual price is determined by the supply demand relationships for these two markets. Feedstock cost contributes about 60% of the total manufacturing cost. The market price of carbon black is strongly dependent on the feedstock cost as shown in Figure 8.

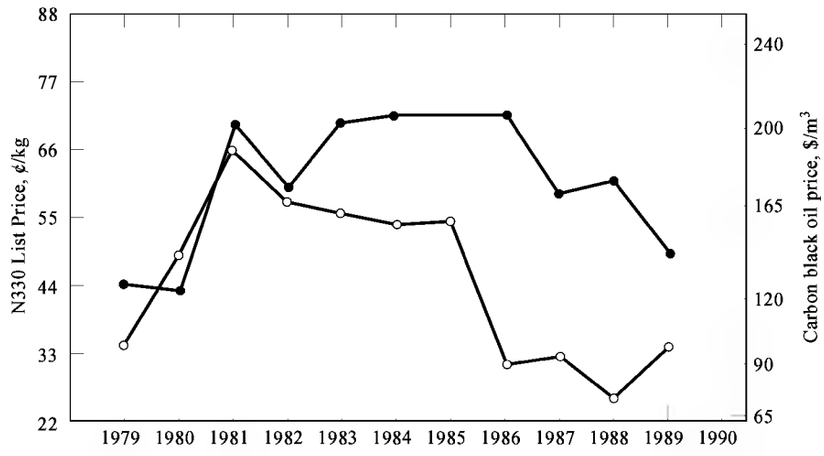

Fig. 8. Carbon black price and raw material cost in the United States (1979–1989). Average U.S. list price N330 (HAF)-grade carbon black, ¢ kg. To convert $ m^3 to $ barrel, multiply by 0.159.

Reactors. The heart of a furnace black plant is the furnace or reactor where carbon black formation takes place under high temperature, partial combustion conditions. The reactors are designed and constructed to be as trouble-free as possible over long periods of operation under extremely aggressive conditions. They are monitored constantly for signs of deterioration in order to ensure constant product quality. The wide variety of furnace black grades for rubber and pigment applications requires different reactor designs and sizes to cover the complete range, though closely related grades can be made in the same reactor by adjusting input variables. Reactors for higher surface area and reinforcing grades operate under high gas velocities, temperatures, and turbulence to ensure rapid mixing of reactant gases and feedstock. Lower surface area and less reinforcing grades are produced in larger reactors at lower temperatures, lower velocities, and longer residence time. Table 3 lists carbon formation temperatures, residence times, and maximum velocities for the complete surface area range of rubber-grade blacks. The N-series designation is in accordance with ASTM D1765, which is the standard classification system for carbon blacks used in rubber products (15). At least three different reactor designs must be used to make this range of furnace blacks and thermal black.

Table 3. Time–Temperature–Velocity Conditions in Carbon Black Reactors[a]

	Surface area, m^2 g	Temperature, °C	Residence time, s	Maximum velocity, m s
N100 series, SAF[b]	145	1800	0.008	
N200 series, ISAF[b]	120		0.010	180–400
N300 series, HAF[c]	80	1550	0.031	
N500 series, FEF[d]	42		1.0	30–80
N700 series, SRF[e]	25	1400	1.5	0.5–1.5
N990 thermal	8	1200–1350	10	10

[a] These characteristic conditions and values depend on reactor designs and fuel rates.

[b] SAF = super abrasion furnace; ISAF = intermediate super abrasion furnace.

[c] HAF = high abrasion furnace.

[d] FEF = fast extrusion furnace.

[e] SRF = semireinforcing furnace.

Reactors are built to have three fairly well-defined zones. Gas and air are introduced into an upstream, primary combustion zone. For reinforcing grades, this connects with a mixing zone of high velocity and turbulence where feedstock is introduced as a fine atomized spray. The mixing zone is followed by a reaction zone of cylindrical shape where carbon-forming reactions occur. Downstream of the reaction zone is a water quench. For high surface area blacks the reactors may have a 15 to 38 cm diameter mixing zone with lengths up to five m. For lower area blacks the reactors are cylindrical with diameters of 75 cm or more and lengths of 9 to 12 m. There is a wide variety of reactors, and each manufacturer has proprietary designs. Air and gas may be introduced to the primary combustion zone either axially, tangentially, or radially. The feedstock can be introduced into the primary flame either axially or radially in the high velocity section of the mixing zone. The high velocity section may be venturi-shaped or consist of a narrow diameter choke. The reactors have a steel shell construction lined with high temperature-resistant castable refractories and insulating cements. The refractories have a service life of one to three years. Figures 9 and 10 show the designs of commercial reactors based on the patent literature.

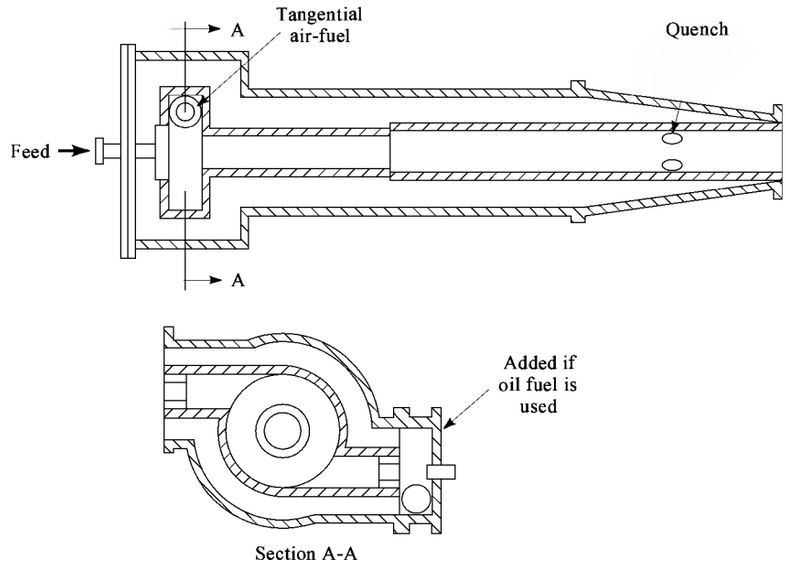

Fig. 9. Reactor for HAF-ISAF (N300-N200) carbon blacks.

Courtesy of Phillips Petroleum Co.

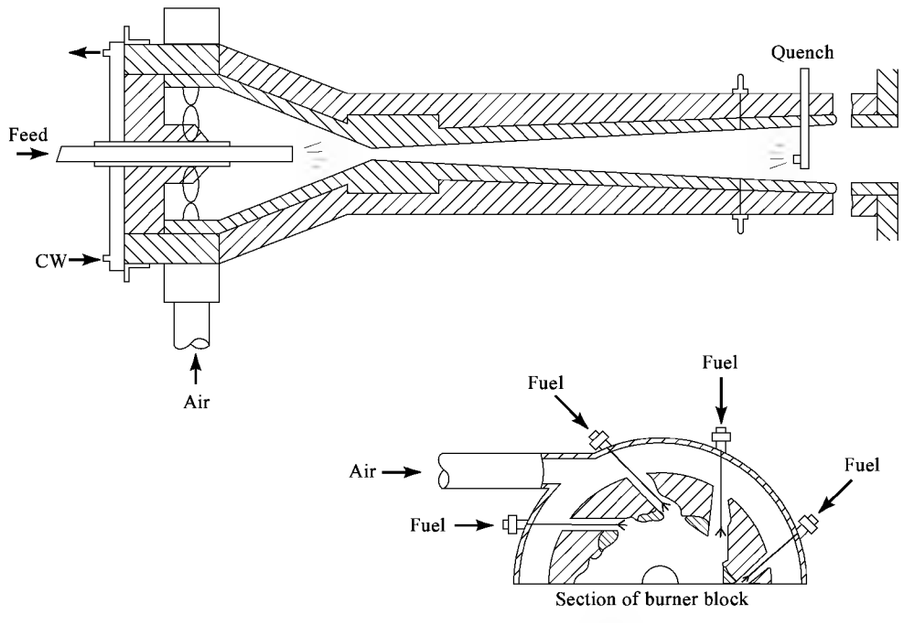

Fig. 10. Columbian reactor for tread blacks. CW cold water.

The quality and yield of carbon black depends on the quality of the feedstock, reactor design, and input variables. The structure is controlled by the addition of alkali metals to the reaction or mixing zones. Usual practice is to use aqueous solutions of alkali metal salts such as potassium chloride or potassium hydroxide sprayed into the combustion chamber or added to the make oil in the oil injector. Alkaline-earth compounds such as calcium acetate that increase the specific surface area are introduced in a similar manner.

The energy utilization in the production of one kilogram of oil-furnace carbon black is in the range of 9.3–16 × 10^7 J (4–6.9 × 10^4 Btu lb), and the yields are 300–660 kg m^3 (2.5–5.5 lb gal) depending on the grade. The energy inputs to the reactor are the heat of combustion of the preheated feedstock, heat of combustion of natural gas, and the thermal energy of the preheated air. The energy output consists of the heat of combustion of the carbon black product, the heat of combustion and the sensible heat of the tail gas, the heat loss from the water quench, heat loss by radiation to atmosphere, and the heat transferred to preheat the primary combustion air. The energy balance for a N300 type of reinforcing grade is shown in Table 4. In this example the thermal efficiency of the process (without tail gas utilization) is 37% for a carbon yield of 0.63 kg L (5 lb gal), 61% based on feedstock.

Table 4. Energy Balance for Reinforcing Grade of Carbon Black

Energy input	
energy from feedstock (288°C preheat)	73%
energy from natural gas	23%
air preheat (400°C)	4%
Energy output	
carbon product (heat of combustion)	37%
tail gas (heat of combustion and sensible heat)	39%
heat loss from water quench	14%
heat loss to atmosphere	6%
air preheat (400°C)	4%

THERMAL BLACK PROCESS

Thermal black is a large particle size, low structure carbon black made by the thermal decomposition of natural gas, coke oven gas, or liquid hydrocarbons in the absence of air or flames. Its use in the United States in 1989 was estimated at about 54–68 million kg or about 4% of total consumption. Although at one time, based on cheap natural gas, thermal black was the least expensive of the regular rubber-grade blacks, it is today the most expensive. It is used in rubber and plastics applications for its unique properties of low hardness, high extensibility, low compression set, low hysteresis, and excellent processing. Its main uses are in O-rings and seals, hose, tire innerliners, V-belts, other mechanical goods, and in cross-linked polyethylene for electrical cables.

The thermal black process dates from 1922. The process is cyclic using two refractory-lined cylindrical furnaces or generators about 4 m in diameter and 10 m high. During operation, one generator is being heated with a near stoichiometric ratio of air and off-gas from the make generation whereas the other generator, heated to an average temperature of 1300°C, is fed with natural gas. The cycle between black production and heating is five minutes alternating between generators, resulting in a reasonably continuous flow of product and off-gases to downstream equipment. The effluent gas from the make cycle, which is about 90% hydrogen, carries the black to a quench tower where water sprays lower the temperature before entering the bag filter. The effluent gas is cooled and dehumidified in a water scrubber for use as fuel in the heating cycle. The collected black from the filters is conveyed to a magnetic separator, screened, and hammermilled. It is then bagged or pelletized. The pelletized form is bagged or sent to bulk loading facilities. The yield is about 45% of the total carbon content of the process gas with an energy utilization of 2×10^8 J kg (0.85×10^5 Btu lb).

ACETYLENE BLACK PROCESS

The high carbon content of acetylene (92%) and its property of decomposing exothermically to carbon and hydrogen make it an attractive raw material for conversion to carbon. Acetylene black is made by a continuous decomposition process at an atmospheric pressure of 800–1000°C in water-cooled metal retorts lined with refractory. The process consists in feeding acetylene into the hot reactors. The exothermic reaction is self-sustaining and requires water cooling to maintain a constant reaction temperature. The carbon black-laden hydrogen stream is then cooled followed by separation of the carbon from the hydrogen tail gas. The tail gas is either flared or used as fuel. After separation from the gas stream acetylene black is very fluffy with a bulk density of only 19 kg m^3 (1.2 lb ft^3). It is difficult to compact and resists pelletization. Commercial grades are compressed to various bulk densities up to 200 kg m^3 (12.5 lbs ft^3).

Acetylene black is very pure with a carbon content of 99.7%. It has a surface area of about 65 m^2 g, an average particle diameter of 40 nm, and a very high but rather weak structure with a DBPA value of 250 mL 100 g. It is the most crystalline or graphitic of the commercial blacks. These unique features result in high electrical and thermal conductivity, low moisture absorption, and high liquid absorption.

A significant use of acetylene black is in dry cell batteries where it contributes low electrical resistance and high capacity. In rubber it gives electrically conductive properties to heater pads, tapes, antistatic belt drives, conveyor belts, and shoe soles. It is also useful in electrically conductive plastics such as electrical magnetic interference (EMI) shielding enclosures. Its contribution to thermal conductivity has been useful in rubber curing bags for tire manufacture. Production capacity for acetylene black in the United States in 1989 was 2.07 million kg from a single plant.

LAMPBLACK PROCESS

The lampblack process has the distinction of being the oldest and most primitive carbon black process still being practiced. The ancient Egyptians and Chinese employed techniques similar to modern methods collecting the lampblack by deposition on cool surfaces. Basically, the process consists of burning various liquid or molten raw materials in large, open, shallow pans 0.5 to 2 m in diameter and 16 cm deep under brick-lined flue enclosures with a restricted air supply. The smoke from the burning pans passes through low velocity settling chambers from which the carbon black is cleared by motor-driven ploughs. In more modern installations the black is separated by cyclones and filters. By varying the size of the burner pans and the amount of combustion air, the particle size and surface area can be controlled within narrow limits. Lampblacks have similar properties to the low area oil-furnace blacks. A typical lampblack has an average particle diameter of 65 nm, a surface area of 22 m^2 g, and a DBPA of 130 mL 100 g. Production is small, mostly in Western and Eastern Europe. Its main use is in paints, as a tinting pigment where blue tone is desired. In the rubber industry lampblack finds some special applications.

IMPINGEMENT (CHANNEL, ROLLER) PROCESS BLACKS

From World War I to World War II the channel black process made most of the carbon black used worldwide for rubber and pigment applications. The last channel black plant in the United States was closed in 1976. Operations still exist and are even being expanded in Europe. The demise of channel black was caused by environmental problems, cost, smoke pollution, and the rapid development of oil-furnace process grades that were equal or superior to channel black products particularly for use in synthetic rubber tires.

The name channel black came from the steel channel irons used to collect carbon black deposited by small natural gas flames impinging on their surface iron channels. Highly aromatic anthracene oils are used as raw material instead of natural gas. The black is scraped off the rollers, and the off-gases from the steel box enclosed rollers are passed through bag filters where additional black is collected. About half of the black is deposited on the rollers. The purified exhaust gases are vented to the atmosphere. The oils used in this process are high boiling and must be vaporized and conveyed to the large number of small burners by means of a combustible carrier gas. Yield of rubber-grade black is 60% and 10–30% for high quality color grades.

The characteristics of roller process impingement blacks are basically similar to those of channel blacks. They have an acidic pH, a volatile content of about 5%, surface area of about 100 m^2 g, and an average particle diameter of 10–30 nm. The smaller particle size grades are used as color (pigment) blacks, and the 30-nm grade is used in rubber.

Characterization and Test Methods

Carbon blacks differ in particle or nodule size, surface area, aggregate size, and aggregate morphology. Surface activity is also a factor in performance, but this feature has been difficult to define or measure. The ultimate dispersible units are aggregates. Aggregate size distribution and morphology determine such properties as surface area, dibutyl phthalate absorption (DBPA), and testing strength. A complete review of the physicochemical characterization of carbon black has been published (21).

Particle Size. The electron microscope is the universally accepted instrument for measuring particle size, aggregate size, and aggregate morphology. Typical electron micrographs of rubber-grade carbon blacks are shown in Figure 11. The grades are classified according to the ASTM D1765 system (2). The first letter N represents a normal rate of cure in rubber, and the first digit represents the average particle size of the carbon black. The last two digits are arbitrarily assigned. Thus N330 is a normal curing grade with a particle diameter range of 26 to 30 nm.

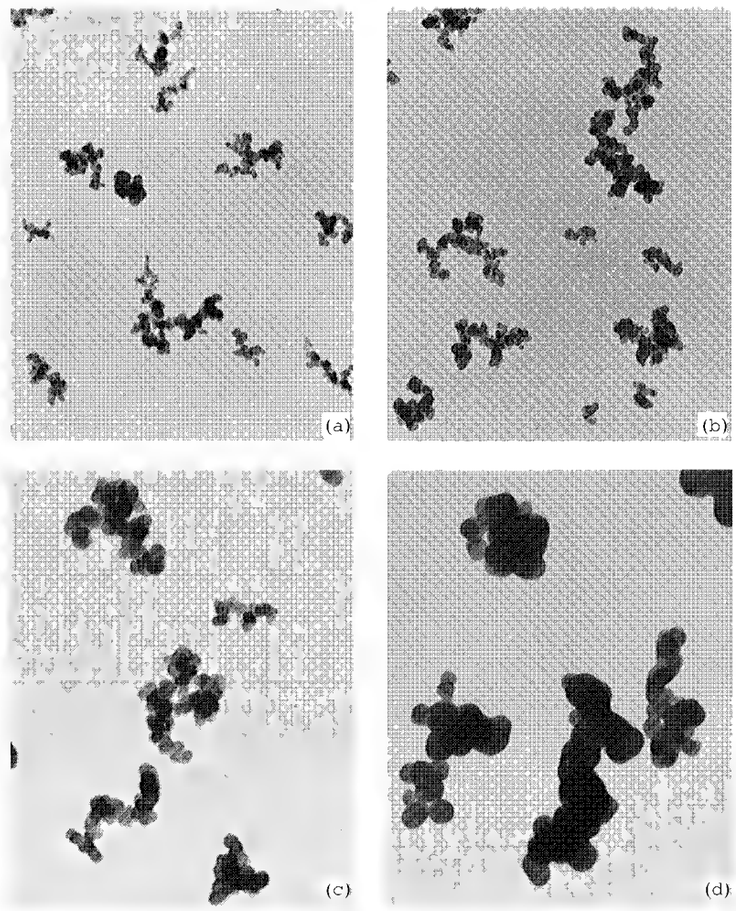

Fig. 11. Electron micrographs of rubber-grade carbon blacks where (**a**) is N110, (**b**) is N220, (**c**) is N550, and (**d**) is N762.

Particle size measurements are made from a negative enlarged to 100,000 diameters (29). Automated image analyzers provide measurements of a variety of particle and aggregate parameters. Surface areas can be calculated from electron microscope measurements. These are in satisfactory agreement with surface areas determined by nitrogen adsorption measurements. Special pigment blacks and blacks used for electrical conductivity are highly porous, and the surface areas calculated from their particle diameters are very much smaller than those calculated from gas absorption.

Surface Area. The most important features influencing the performance of carbon blacks are aggregate size and surface area. Surface area is measured by gas- and liquid-phase adsorption techniques, and depends on the amount of adsorbate required to form a surface monolayer. If the area occupied by a single-adsorbate molecule is known, a simple calculation will yield the surface area. A low temperature nitrogen absorption method, based on the original method of Brunauer, Emmett, and Teller (BET) (30), has been adopted by ASTM as standard method D3037-86 (2).

Liquid-phase adsorption methods are widely used for quality control and specification purposes. The adsorption of iodine from potassium iodide solution is the standard ASTM method D1510-83 (2). The surface area is expressed as the iodine number whose units are milligrams of iodine adsorbed per gram of carbon. It is quite fortuitous that the values of iodine numbers turn out to be about the same as the values for surface areas in square meters per gram by nitrogen adsorption for nonporous carbon blacks.

Another standard industry method for surface area is based on the adsorption of cetyltrimethylammonium bromide (CTAB) from aqueous solution. This is ASTM method D3765-85 (2). This method measures the specific surface area of carbon black exclusive of the internal area contained in micropores that are too small to admit the large CTAB molecules. For rubber-grade nonporous blacks the CTAB method gives excellent agreement with nitrogen surface areas.

Structure and Aggregate Morphology. Structure or aggregate morphology is another important characteristic that influences performance. Structure is determined by aggregate size and shape. These properties affect aggregate packing and the volume of voids in the bulk material. In liquid media structure affects rheological properties such a viscosity and yield point. In rubber, viscosity, extrusion die swell, modulus, and electrical conductivity are affected by structure. For classification and quality control purposes structure is assessed by measurements of void volume, either in the bulk by density or by the absorption of a liquid such as dibutyl phthalate (DBP). The dibutyl phthalate absorption number determination is ASTM method D2414-86 (2). The void volume in the bulk is usually measured under pressure. From the bulk density under a given pressure the volume of voids per unit weight of carbon is calculated.

Tint Strength. Tint strength is another industry method used for the classification of carbon blacks adopted by ASTM as D3265-85 (2). Tint strength is closely related to surface area and decreases with increasing aggregate size. It provides a rough estimate of the reinforcing potential of carbon black in rubber. In this test a small amount of carbon black is mixed with zinc oxide and an oil vehicle to produce a black or gray paste. The reflectance of this paste is measured and compared to the reflectance of a paste made with a reference black. The ratio of the reference black paste reflectance to the sample black multiplied by 100 is the tint strength.

There are many other test methods used to characterize carbon blacks for quality control and specification purposes. Table 5 lists some of these methods which, with a few exceptions, have been adopted by ASTM.

Table 5. Special Analytical Test Methods for Carbon Black

Test method	Standard	Comment
iodine adsorption, mg g	ASTM D1510	amount of iodine adsorbed from aqueous solution as a measure for the specific surface area; not applicable for oxidized or highly porous carbon blacks
N_2 surface area, m^2 g	ASTM D3037	calculated from amount of adsorbed N_2 at liquid nitrogen temperature
CTAB surface area, m^2 g	ASTM D3765	amount of cetytrimethylammonium bromide adsorbed from aqueous solution as measure of specific nonporous (outer) surface area
aggregate dimension	ASTM D3849	determination of aggregate dimensions (unit length, width, etc) by

		electron microscope image analysis
aggregate size distribution		diameters of equivalent solid spheres that sediment at same rate as aggregates during centrifuging
DBP absorption, mL 100 g	ASTM D2414	determination of the void volume with dibutyl phthalate in a special kneader as measure of structure
void volume, mL 100 g		volume of voids from bulk density measurement under pressure
24M4-DBP absorption, mL 100 g	ASTM D3493	determination of DBP absorption after four repeated compressions at 165 MPa (24,000 psi)
jetness		light absorption of a carbon black paste in linseed oil; determination by visual comparison against standard blacks or by measuring the absolute light emission
tint strength, %	ASTM D3265	ability of a carbon black to darken a white pigment in a linseed oil paste; the tinting strength is the weight percentage of the standard carbon black with respect to the tested black to obtain the same gray tone; different standard white pigments and carbon black concentrations are used according to ASTM
volatiles, %	ASTM D1620	weight loss when calcined at 950°C for 7 min
heating loss (moisture), %	ASTM D1509	weight loss on drying at 125°C for 1 h
pH	ASTM D1512	pH of an aqueous slurry of carbon black; pH is mainly influenced by surface oxides
extractables, %		amount of material which can be extracted by a boiling solvent, usually toluene, in at least 8 h
	ASTM D3392	light absorption–transmission of a 1,2-dichlorobenzene solution of the extracted material
ash content, %	ASTM D1506	amount of noncombustible material after burning the carbon black at 675°C
sulfur content, %	ASTM D1619	
sieve residue, %	ASTM D1514	amount of coarse impurities that cannot be purged through a testing sieve by water
bulk density, g L	ASTM D1513	measure for the densification of carbon black
tamped density, g L		similar to bulk density; however, void volume is reduced by tamping
pellet size distribution	ASTM D1511	determination by means of sieve shaker
fines content, %	ASTM D1508	only for pelletized blacks; percentage passing through a sieve of 125 μm (mesh) width

Grades and Applications

U.S. consumption of carbon black in 1988 by various market sectors is shown in Table 6. About 90% of total consumption is in the rubber industry and 69% for tires. About 10% is consumed for other automotive products and 11% for rubber products unrelated to the automotive industry. The automotive industry accounts for 79% of consumption. Pigment applications account for about 10% of consumption, most of this for plastics and printing inks. Western Europe consumes 74% in tires and other automotive products and almost 20% in other industrial rubber products. Pigment applications in Western Europe and Japan are 5–6% of consumption.

Table 6. U.S. End Use Consumption of Carbon Black[a]

Market sector	Consumption, 10^3 t	Percent of total, %
Rubber		
tires, treads, tubes	927	68.9
other automotive	132	9.8
molded, extruded, industrial products, roofing, etc	148	10.9
Total rubber	*1207*	*89.6*
Nonrubber		
plastics	59	4.4
printing inks	48	3.6
paint	9	0.7
paper	7	0.5
other	16	1.2
Total nonrubber	*139*	*10.4*

[a] 1988.

Rubber Goods. A selected list of typical properties, taken from ASTM D1765 of rubber-grade carbon blacks (2), is shown in Table 7. In addition to the assigned ASTM N-numbers, the list includes the old letter designations, pour densities, structure (DBPA), surface areas, and tint data. The structure area relationships of these grades, called the carbon black spectrum, is illustrated in Figure 12, which shows a diagram of DBPA values versus the nitrogen surface areas. Closely related grades are easily distinguished. A broad range of structure is available in the N700-N600 and N300 range of surface areas. Table 8 lists the principal rubber grades by their N-number classification, general rubber properties, and typical uses. The behavior of different grades is dominated mainly by surface area and structure (DBPA). High surface area produces high reinforcement as reflected in high tensile and tear strengths, high resistance to abrasive wear, higher hysteresis, and poorer dynamic performance. A present day challenge to carbon black technologists is to optimize the balance between tire wear and tire hysteresis or the rolling resistance. Some progress on this problem has been made by using new furnace designs and other process variables that broaden the aggregate size distributions and lower the tint strength while maintaining surface area, structure, and reinforcement (31,32).

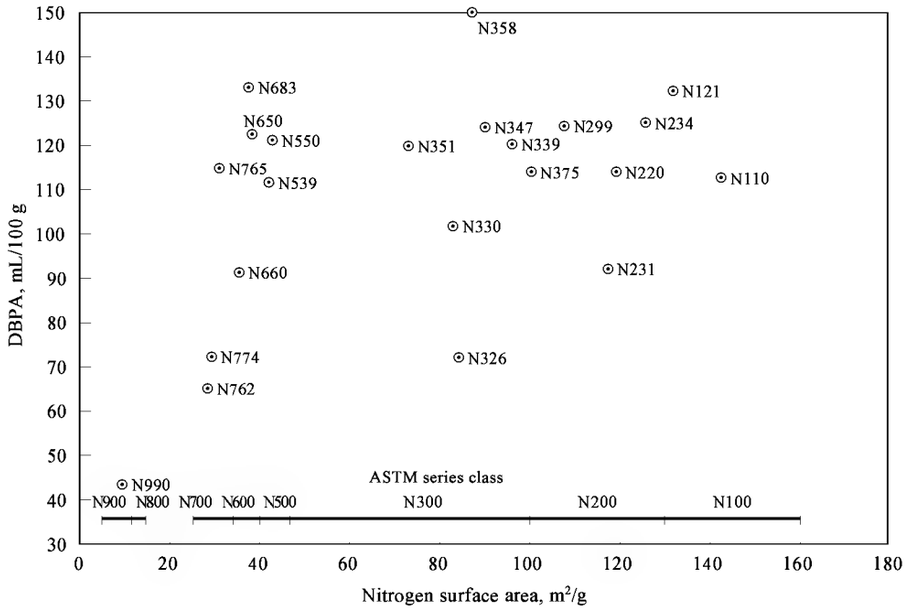

Fig. 12. Rubber grades carbon black spectrum.

Table 7. Typical Properties Rubber-Grade Carbon Blacks[a]

ASTM designation	Former industry designation[b]	I_2 absorption number (D1510), g kg	DBPA[c] (D2414), mL 100 g	DBPA[c] (compressed sample) (D3493), mL 100 g	CTAB[d] surface area (D3765), m^2 g	Nitrogen surface area (D3037), m^2 g	Tinting strength (D3265)	Pour density (D1513), kg m^3
N110	SAF	145	112	98	126	143	124	335
N121	SAF-HS	121	132	112	121	132	121	320
N220	ISAF	121	114	100	111	119	115	345
N231	ISAF-LM	121	92	86	108	117	117	390
N234	ISAF-HS	120	125	100	119	126	124	320
N299	ISAF-HS	108	124	105	104	108	113	335
N326	HAF-LS	82	72	69	83	84	112	465
N330	HAF	82	102	88	83	83	103	375
N339	HAF-HS	90	120	101	95	96	110	345
N347	HAF-HS	90	124	100	88	90	103	335
N351	HAF-HS	68	120	97	74	73	100	345
N358	HAF-HS	84	150	112	88	87	99	290
N375	HAF-HS	90	114	97	98	100	115	345
N539	FEF	43	111	84	41	41	0	385
N550	FEF	43	121	88	42	42	0	360
N650	GPF-HS	36	122	87	38	38	0	370
N660	GPF	36	90	75	35	35	0	425
N683	GPF-HS	35	133	0	39	37	0	335
N762	SRF	27	65	57	29	28	0	505
N765	SRF-HS	31	115	86	33	31	0	375
N774	SRF	29	72	62	29	29	0	495
N990	MT	0	43	40	9	9	0	0

[a] ASTM D1765.

[b] SAF = super abrasion furnace; ISAF = intermediate super abrasion furnace; HAF = high abrasion furnace; FEF = fast extrusion furnace; GPF = general purpose furnace; SRF = semireinforcing furnace; MT = medium thermal; HS = high structure; LS = low structure; LM = low modulus.

[c] Dibutyl phthalate *[84-74-2]* absorption.

[d] Cetyl trimethylammonium bromide *[57-09-0]*.

Table 8. Applications of Principal Rubber-Grade Carbon Blacks

Designation	General rubber properties	Typical uses
N110, N121	high abrasion resistance	special tire treads, airplane, off-the-road racing
N220, N299, N234	high abrasion resistance, good processing	passenger, off-the-road, special service tire treads
N339, N347, N375, N330	high abrasion resistance, easy processing, good abrasion resistance	standard tire treads, rail pads, solid wheels, mats, tire belt, sidewall, carcass retread compounds
N326	low modulus, good tear strength, good fatigue, good flex cracking resistance	tire belt, carcass, sidewall compounds, bushings, weather strips, hoses
N550	high modulus, high hardness, low die swell, smooth extrusion	tire innerliners, carcass, sidewall, innertubes, hose, extruded goods, v-belts
N650	high modulus, high hardness, low die swell,	tire innerliners, carcass, belt, sidewall

	smooth extrusion	compounds, seals, friction compounds, sheeting
N660	high modulus, high hardness, low die swell, smooth extrusion	carcass, sidewall, bead compounds, innerliners, seals, cable jackets, hose, soling, EPDM compounds
N762	high elongation and resilience, low compression set	mechanical goods, footwear, innertubes, innerliners, mats

The consumption of the various carbon black grades can be divided into tread grades for tire reinforcement and nontread grades for nontread tire use and other rubber applications. Table 9 shows the distribution of production of types for these uses. In the United States 55% production is for tread grades. In Western Europe tread-grade production is 64%, and in Japan it is 60%.

Table 9. Carbon Black Production[a] by Grade, 10^3 t

	United States	Western Europe	Japan
N100	35	28	37.1
N200	158	161	118
N300	555	528	300
Total tread grades	*748*	*717*	*418*
percent	55.2	63.8	59.5
N500	120	153	136
N600	326	137	87
N700	129	103	29
N900 (thermal)	23		9
Total nontread grades	*598*	*393*	*261*
percent	44.1	35.0	37.1
other grades			
acetylene	9.1	14	24
Total carbon black	*1355*	*1124*	*703*

[a] 1988.

Special-Grade Carbon Blacks. In 1988 over 10% of U.S. consumption of carbon black was for nonrubber applications, ie, special blacks. In Europe and Japan about 5% is consumed for these uses. Most of the special black grades are manufactured by methods to meet specific product specifications required for their end uses. They sell for a higher average price than the rubber grades. These markets have been growing at an average annual rate twice that of the rubber black grades. Of increasing importance in recent years have been applications in plastics to improve weathering resistance and to impart antistatic and electrically conductive properties.

About 42% of special blacks are used in plastics, 35% in printing inks, 7% in paper, and 16% in miscellaneous applications. News inks account for most of the printing ink market. Electrical applications have been taking an increasing share of the plastics market. Medium and high color grades, in their normal and surface-oxidized versions, are used in enamels, lacquers, and plastics for their extreme jetness. Typical properties of special grades of furnace blacks are listed in Table 10. The list is divided into normal furnace grades and surface oxidized grades. Increased surface oxidation decreases viscosity, improves dispersion, and increases the flow behavior in many liquid systems. The volatile content is an indication of the degree of surface oxidation. To improve dispersion and flow, special blacks generally are produced at lower structural (DBPA) and bulk density values than rubber-grade carbon blacks.

Table 10. Furnace Process Special Grades for Pigment Applications in Inks, Plastics, Paints, and Paper

Industry classification	N_2 surface area, m^2 g	Particle diameter, nm	DBPA[a], mL 100 g		Bulk density, g L		Nigrometer[b] index	Tinting strength	Volatile, %	pH
			Fluffy	Pellets	Fluffy	Pellets				
high color	250–300	14–15	70–75	60–65	50–300	400–550	65–76	117–124	1.2–2.0	7–10
medium color	150–220	16–24	47–122	46–117	130–300	390–550	74–78	118–124	1.0–1.5	8–10
regular color	45–140	20–37	42–125	42–124	176–420	350–600	84–93	73–119	0.9–1.5	6–10
low color	25–45	41–75	71	64–120	256	352–512	94–99	48–69	0.6–0.9	8–10
				Surface oxidized grades						
high color	400–600	10–20	121	105			64	100–135	8.0–9.5	2.0–3.3
medium color (long flow)	100–38	23–24	49–60	55	240–360	530	83–84	112–135	3.5–5.0	2.5–4.0
medium color (medium flow)	96–110	25	49–72	70	225–360	480	84	112–114	2.5–3.5	4.0–4.5
low color	30–40	50–56	48–93		260–500		92–100	64	3.5	3.0

[a] Dibutyl phthalate absorption.

[b] A method for measuring the diffuse reflectance from a black paste with a black tile standard. The low numbers represent the jettest or most intense black grades.

Table 11 lists the types and applications of special pigment-grade carbon blacks. Included in this list are thermal black and lampblack. Over 40 special black grades have been developed based on the furnace process having a broad range of surface areas, from 20 m^2 g to over 1500 m^2 g. The lower surface area products are used in printing inks and tinting. The high area, more expensive products find use in high color enamels and lacquers.

Table 11. Types and Applications of Special Pigment Grades of Carbon Blacks

Type	Surface area, m^2 g	DBPA[a], mL 100 g	Volatile content, %	Uses
		Normal grades		

high color	230–560	50–120	2	high jetness for alkyl and acrylic enamels, lacquers, and plastics
medium color	220–220	70–120	1–1.5	medium jetness and good dispersion for paints and plastics; ultraviolet and weathering protection for plastics
regular color	80–140	60–114	1–1.5	for general pigment applications in inks, paints, plastics, and paper; gives ultraviolet protection in plastics, high tint, jetness, gloss, and dispersibility in inks and paints
	46	60	1.0	good tinting strength, blue tone, low viscosity; used in gravure and carbon paper inks, paints, and plastics
	45–85	73–100	1.0	main use is in inks; standard and offset news inks
low color	25–42	64–120	1.0	excellent tinting black-blue tone; used for inks-gravure, one-time carbon paper inks; also for paints, sealants, plastics, and cements
thermal blacks	7–15	30–35	<0.5	tinting-blue tone; plastics and utility paints
lamp blacks	20–95	100–160	0.4–0.9	paints for tinting-blue tone
			Surface oxidized grades	
high color	400–600	105–121	8.0–9.5	used for maximum jetness in lacquers, coatings, plastics, fibers, record disks
medium color, long flow	138	55–60	5	used in lithographic, letterpress, carbon paper, and typewriter ribbon inks; high jetness, excellent flow, low viscosity, high tinting strength, gloss, and good dispersability
medium color, long flow	96	70	2.5	used for gloss printing and carbon paper inks; excellent jetness, dispersibility; tinting strength, and gloss in paints
low color	30–40	48–93	3.5	used for tinting where flooding is a problem; easy dispersion

[a] Dibutyl phthalate absorption.

Electrically Conductive Grades. An important application of carbon black is to produce electrically conductive and antistatic polymer composites. These applications include antistatic carpet backing and floor tile, electrical heating elements, high voltage cable semiconductive shields, video tapes and disks, and EMI shielding. The electrical conductivity of bulk carbon black under compression is in the range of 0.02 to 0.5 ohm·cm. The conductivity of conductive carbon black-filled rubber and plastics is in the range of 1 to 10^8 ohm·cm. There is no clear relationship between bulk black conductivity and compound conductivity. The main variable determining compound conductivity is the carbon black concentration. At high enough concentrations all carbon blacks can produce compound resistivities of about 1.0 ohm·cm. For superconductive carbon black this concentration is 7–8% and for thermal black the required concentration is 65–70%. Figure 13 shows the concentration resistivity relationships of selected carbon blacks covering the complete range of rubber and conductive grades (33). It can be seen that there is a critical concentration for each grade of carbon black above which the resistivity drops precipitously. This is often referred to as the percolation concentration.

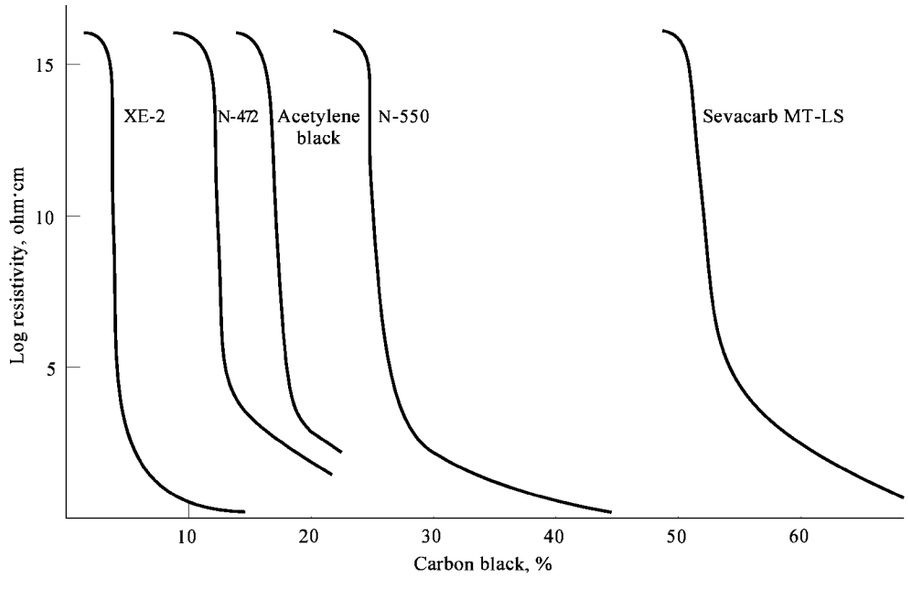

Fig. 13. Electrical resistivity versus carbon black concentration.

The main carbon black characteristics determining its conductive behavior are surface area, aggregate morphology, and degree of graphitization or crystallinity. The high conductivity of acetylene black is attributed to its highly developed structure and its crystallinity. High conductivity furnace-grade blacks have very high surface areas and structures (DBPA). Superconductive blacks, byproducts of synthesis gas manufacture, have very high surface areas, highly developed structures, and a high degree of crystallinity.

The effect of surface area on conductivity was shown for channel-grade blacks in 1949 (34) and the surface area relationship to conductivity for furnace blacks in 1954 (35). High surface area is associated with increasing surface roughness and internal porosity rather than decreased particle or nodule size. Because of the decreased density of the aggregates resulting from the porosity of high surface area conductive blacks, they possess a larger number of aggregates per unit weight. At a given weight concentration, closer packing of aggregates increases conductivity. Crystallinity increases with high porosity contributing to high conductivity. The crystallinity increase results from the burnout of the more amorphous regions of the aggregate during manufacture.

The mechanism of electrical conduction in composites occurs by a process of electron tunneling through the polymer phase (36). Electrons tunnel from the black aggregates to their nearest neighbor. The resistivity of vulcanizates is a function of the average distance between aggregates (37). In addition to carbon black concentration, this gap distance depends on particle size, surface area, and aggregate morphology.

There are a number of publications on the properties and applications of electrically conductive carbon blacks (38–40). Figure 14 shows the electron micrographs of two grades of electrically conductive carbon blacks. The furnace blacks have the particle size of N200-N300 types. Their high surface areas indicate high internal porosity. Table 12 shows typical data and uses for eight electrically conductive grades of carbon black and by-product carbons. The

large differences between the nitrogen surface areas and the areas measured by cetyltrimethyl-ammonium bromide (CTAB) absorption are because of internal porosity. The CTAB molecules are so large that they do not penetrate the pores available to the nitrogen molecules. The large, bulky aggregates, the high porosities, and low aggregate densities of the electrical grades produce high DBPA values, much larger than for normal furnace blacks.

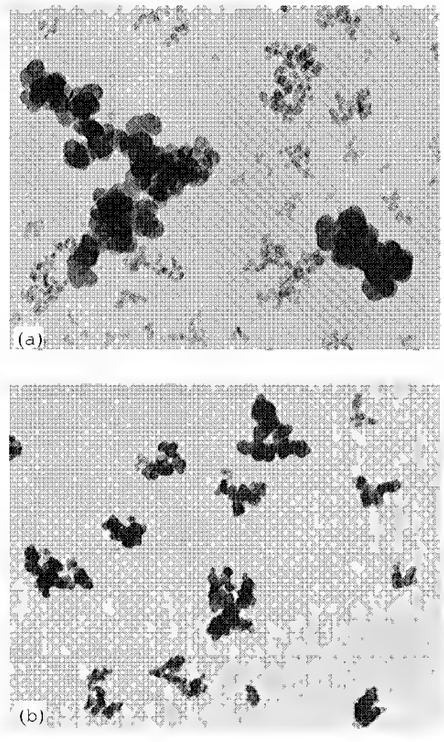

Fig. 14. Electron micrographs of electrically conductive grades of carbon black where (**a**) is Vulcan XC-72 (Cabot) (100,000 ^) and (**b**) is Vulcan P (Cabot) (100,000 ^).

Table 12. Typical Data and Uses for Electrically Conductive Grades of Carbon Blacks

Type	Particle diameter, nm	N_2 Surface area, m^2 g	CTAB Surface area, m^2 g	DBPA[a] mL 100 g	Tinting strength, D3265	Uses
acetylene black	42	64		300	52	high voltage semiconductive shields, conductive rubber, and plastics
conductive furnace (CF)N293	22	145	114	100	117	conductive rubber and plastics, carpet backing
conductive furnace (CF)N742	22	270	145	178	82	conductive and antistatic rubber and plastics products
		1475		330	163	
superconductive furnace (SCF)		1000		245		electromagnetic interference shielding (EMI) compounds, videodisks, tapes, etc
	30	800		365	124	
synthesis gas by-product carbon		1000	620	400		EMI, videodisks, PTC[b] compounds (for heating tapes)
		1250		495		

[a] Dibutyl phthalate absorption.

[b] PTC positive temperature coefficient.

Carbon Black Manufacture and Market

Manufacturers and Productions. The consumption of carbon black in the United States reached a peak of 1,506,000 t during the beginning of the oil crisis in 1973. Then consumption decreased to 1,210,000 t in 1989. A number of events have contributed to decreased consumption by the rubber and tire industries including tire radialization, increased tire mileage, downsizing of tires, and increased imports of foreign cars. The negative influence of these events have pretty much run their course, and during the last 10 years there has been a modest growth in carbon black production. Production for the period 1973–1989 is shown in Figure 15.

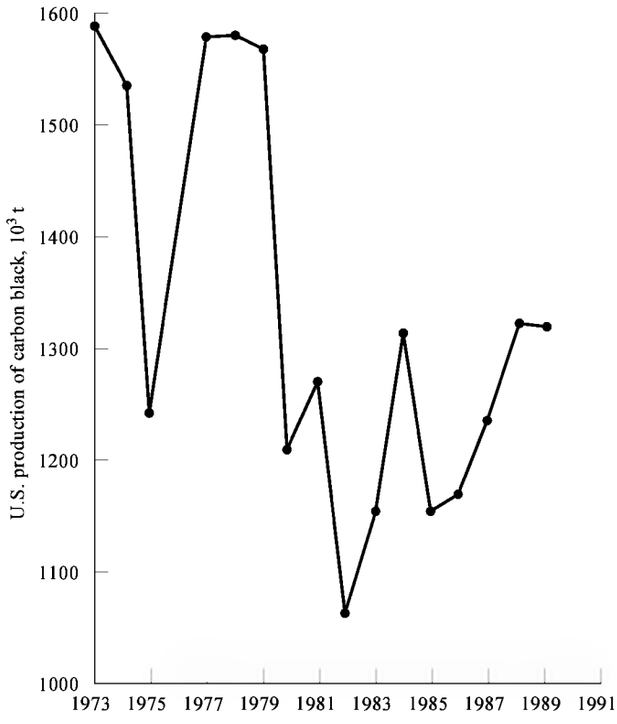

Fig. 15. U.S. production of carbon black (1973–1989).

The shrinkage in demand has resulted in a restructuring of the carbon black-industry. Several of the principal multinational oil companies have left the business including Ashland, Cities Service Co., Phillips, and Conoco. Some plants have changed ownership. In the United States this has increased the production capacities of Degussa, Sid Richardson, and Huber. Today's U.S. industry consists of six principal producers. Rated capacities of the six U.S. manufacturers is shown in Table 13. Cabot Corp. and Columbian Chemicals are the leading producers, followed by Degussa, Sid Richardson, J. M. Huber Corp., and Witco. A survey of the future markets and present structure of the carbon black industry has been presented (1).

Table 13. U.S. Carbon Black Manufacturers Nameplate Capacities, 1988

Manufacturers	Capacity 10^3 t	U.S. capacity, %
Cabot Corp.		
Franklin, La.	153	
Pampa, Tex.	32	
Parkersburg, W.Va.	83	
Ville Platte, La.	126	
Total	*394*	25
Columbian Chemicals		
El Dorado, Ark.	75	
North Bend, La.	121	
Hickok, Kans.	38	
Moundsville, W.Va.	82	
Total	*316*	20
Degussa		
Arkansas Pass, Tex.	82	
Ivanhoe, La.	100	
Belpre, Ohio	55	
Total	*237*	15
Sid Richardson Co.		
Addis, La.	62	
Big Spring, Tex.	57	
Borger, Tex.	125	
Total	*244*	15.5
J. M. Huber Corp.		
Orange, Tex.	62	
Baytown, Tex.	102	
Borger, Tex.—Furnace	57	
Thermal	23	
Total	*244*	15.5
Witco Corp.		
Phenix City, Ala.	25	
Ponca City, Okla.	68	
Sunray, Tex.	46	
Total	*139*	8.8
Total U.S. capacity	*1574*	

World carbon black rated capacities are shown in Table 14. North America has the largest capacity. Europe, Southeast Asia, and Russia Eastern Europe have about equal capacities and Africa and the Middle East have only small production. The growth areas are predicted to be Southeast Asia and the Russia Eastern Europe markets. The capacities for certain areas such as China and Russia Eastern Europe should be taken as rough estimates.

Table 14. World Carbon Black Capacities by Region and Country, 1988

Region	Number of plants	Estimated capacity, 10^3 t
North America		
United States	22[a]	1565[a]
Canada	3[a]	182
Mexico	2	158
Total	*27*	*1095*
South America		
Argentina	1	48
Brazil	3	199
Colombia	2	36
Peru	1	8
Venezuela	1	40
Total	*8*	*331*
Europe		
Great Britain	2	140
France	3	239
Germany	5	385
The Netherlands	2	120
Italy	3	191
Portugal	1	21
Spain	3	104
Sweden	1	33
Total	*20*	*1233*
Australia South East Asia		
Australia	2	76
India	7	153
China[b]	30–45	500
Japan	12	766
South Korea	3	170
Malaysia	1	23
Pakistan	1	10
Philippines	1	15
Taiwan	1	53
Thailand	1	20
Total	*32*	*1786*
Africa	2	75
Middle East		
Iran	1	15
Turkey	1	35
Total	*2*	*50*
Russia Eastern Europe		
Russia[b]	14	1300
Yugoslavia	1	36
Poland		58
Romania		130
Czechoslovakia		64
Total		*1588*
Total world capacity		*6968*

[a] Includes one thermal black plant (capacity, 25,000 t).

[b] Estimate.

Product Safety

The safety aspects of carbon black have been the subject of a number of reviews and articles (41–43). The manufacture of carbon results in trace amounts of organic and inorganic impurities. These impurities have been suspected of causing potential health problems. Of particular concern have been the salts of toxic metals and adsorbed polynuclear aromatic hydrocarbons (PNAs). A few of the polyaromatic hydrocarbons are known to be mutagens and or animal carcinogens. The solvent extract of furnace blacks is in the range of 300 to 2000 ppm (0.03–0.20%). Most of this extract consists of 10–15 organic compounds, the majority of which are not genotoxic. One compound that is toxic is benzo [α] pyrene *[50-32-8]*, BαP, often used as an indicator of potential hazard. BαP ranges from 0 to 50 ppm and is less than one percent of the total extract. There have been a number of studies initiated by the U.S. carbon black industry to examine the health effects of various commercial carbon blacks and their benzene extracts. Tests have been made using laboratory animals. Investigations on absorption and elution effects in stomach fluids and human blood have been conducted. Although the solvent extracts of carbon black do show toxic properties, the aqueous systems of concern in humans show no elution of BαP and no toxic properties. The BαP is believed to be so strongly absorbed on the surface of carbon black and in such high dilution that it is inactive in animal testing for carcinogenicity. Statistical studies on the frequency of cancer of long-term employees in a carbon black plant covering a period of 17 years (1939–1956) has been reported (44). There is no evidence of increased cancer risk from exposure to industrial carbon blacks. The scientific literature based on animal research as well as observations on carbon black plant employees show no evidence of detrimental health effects. Most studies of carbon black dust inhalation and intratracheal administration with animals indicate that carbon black is not carcinogenic. OSHA regulations for carbon black dust concentrations call for an average exposure level over a given time period of not more than 3.5 mg m^3.

Environmental Aspects

The carbon black industry takes extreme efforts to confine product during all stages of manufacture (45). Highly efficient bag filters are used to collect the product. After collection the fluffy carbon black is densified and pelletized to minimize dusting problems during shipping and use.

The process gases from the filters consist of nitrogen, carbon monoxide, carbon dioxide, hydrogen, water, small amounts of hydrogen sulfide, and other sulfur- and nitrogen-containing gases. In the past the process gases have been flared. Process gas is used as a fuel for in-plant heat needs, and where local conditions warrant, it may be burned to generate steam or power.

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DIAMOND, NATURAL

Naturally occurring diamond is a relatively rare polymorphic form of carbon characterized by a three-dimensional arrangement of tetrahedrally coordinated carbon atoms. Both natural and synthesized diamond *[7782-40-3]* have the highest hardness of all known materials, the highest thermal conductivity at room temperature, a high refractive index and optical dispersion, a low thermal expansion, and a relatively high inertness to chemical attack. This unique combination of properties permits diamond to be foremost in certain applications: as a highly prized gemstone; industrially as an important abrasive material unsurpassed in certain cutting, drilling, sawing, machining, grinding, and polishing operations for many materials; and in electronic and optical applications as a heat sink and window material, respectively.

Occurrence and Exploration

Diamonds were first discovered in ancient times in India and Borneo and later in Brazil in 1670 in alluvial deposits where water had sorted minerals on the basis of density and toughness. This type of tumbling often concentrates the better quality crystals such as those found in the ocean off the west coast of Africa. Exploration can be done by stream panning or drilling in conjunction with a search for the heavy mineral assemblages that accompany diamond. Alluvial deposits account for about 40% of the diamond found in primary sources.

Upstream exploration has sometimes led to the discovery of the primary source of alluvial stones, namely, kimberlite "pipes." These structures of igneous origin are the principal source of natural diamonds, and there are over 1000 occurrences of them in the world. Only a small number contain a high enough concentration of diamonds to warrant mining. Even in successful mining operations the ratio of diamond to the gangue that has to be removed and crushed is of the order of one part in a million or even less, of which the proportion of gem quality crystals is about 20%. The first key discovery of diamond-containing pipes was in South Africa in 1867, and these structures are well-known from the publicity given to the Kimberley, Premier, and other mines there. More recent successful discoveries were a producing pipe in Botswana, Africa in 1967 and the Argyle alluvial deposits and pipes in Australia in 1979. Exploration continues in several countries including Canada and the United States for the source of diamonds brought south by the glacier into the United States. Methods include the tracing of certain heavy minerals upstream, drilling, the use of aerial photographs to try to find manifestations of circular pipe structures at the surface, and magnetic anomalies by aerial surveys. There is a pipe in Arkansas where amateurs can dig with a reasonable probability of finding a diamond (1).

The combination of the origin of kimberlite and the enclosed diamonds is still a source of mystery and continued study (2–6). The age of some diamonds has been measured on the basis of certain radioactive elements in silicate inclusions to be over three billion years old with volcaniclike upward intrusion taking place 100 million years ago (2). It seems somewhat anomalous compared to other mineral deposits that in spite of the large size of the natural pressure vessels, the largest diamond ever found, the Cullinan, weighed 3106 carats (~176 cm^3 or 620 g). Only about 33 stones weighing more than 300 carats (60 g) have ever been found (7). The fourth largest rough uncut stone (890 carats) emerged in the market as a stone of 407.48 carats (8). The growth history of each crystal is obviously extremely complex involving intermittent growth and dissolution as revealed by studies of the internal structure (9). There may also have been a problem in maintaining a supply of carbon to the growing crystal over long periods of time, and the dissolution of material during the strenuous trip upward from the stability region of diamond at depth certainly contributed to decreasing the size of some crystals. Overpressure is known to increase the nucleation frequency in synthesized diamond and this might translate to many small crystals at great depths. In any case, it seems quite certain that nature did not use a metal–carbon solution system as in the commercial process for synthesis of diamond at high pressure and temperatures, but the pressure–temperature ranges for both processes may have been comparable, greater than 1000°C and 4.5 GPa (45 kbar) (4,5). This translates to depths of about 150–200 km into the earth.

Diamonds also occur in meteorites, probably as a result of high pressures produced dynamically by impact (10,11). The shock or explosive mode of synthesis is a viable process for fine diamond powders of both the cubic and hexagonal (lonsdaleite) polymorphs (12) naturally or otherwise. Some diamonds in space appear to have formed by processes more closely related to the low pressure chemical vapor deposition processes described later (see CARBONS, DIAMOND, SYNTHETIC) (13).

Recovery

Alluvial diamonds are recovered from streambeds by panning or washing techniques as for heavy minerals or, more productively, by removal from pockets where the water has concentrated them. High quality gemstones are recovered from ocean deposits off the coast of Africa by holding back the water with seawalls long enough to remove a considerable overburden of sand and gravel.

The original mining of the pipes begins at the surface in the softer weathered "yellow" ground, but most of the subsequent recovery is by removal from depth of the harder, unweathered "blue" kimberlite. This material is then crushed for separation of the diamonds by a variety of techniques. One of the more interesting sorting methods is the grease table that takes advantage of the fact that most diamonds will stick to grease but not to water that removes the gangue. There are some diamonds that will not stick to grease but can be separated by electrostatic methods. A more modern method for the separation of crystal from rock uses the emission of light by luminescence of diamond when exposed to x-rays. The stones are then themselves separated mostly by hand into two main categories, gem and industrial, with further classification within each of these categories.

Properties

Not all of the properties of diamond are considered here, and additional information and qualifications are available (9,14–19).

Structure, Density, and Morphology. The lattice constant of the face-centered cubic form of diamond is 0.3567 nm with a density of 3.52 g cm^3. For the hexagonal modification, a 0.252 nm and c 0.412 nm with the same density as the cubic form (Fig. 1). In this allotropic modification the stacking of successive layers is ABABAB ... as compared to the ABCABC ... type of stacking of the normal cubic form. Diamond twins readily during growth on the (111) plane resulting in both interpenetration and flat twins called macles. The growth morphology of natural diamond is often octahedral, but dodecahedral crystals are very common, perhaps because of subsequent solution after growth. Only very small grains (<30 μm) of the hexagonal modification have ever been seen, so not much can be said of their morphology.

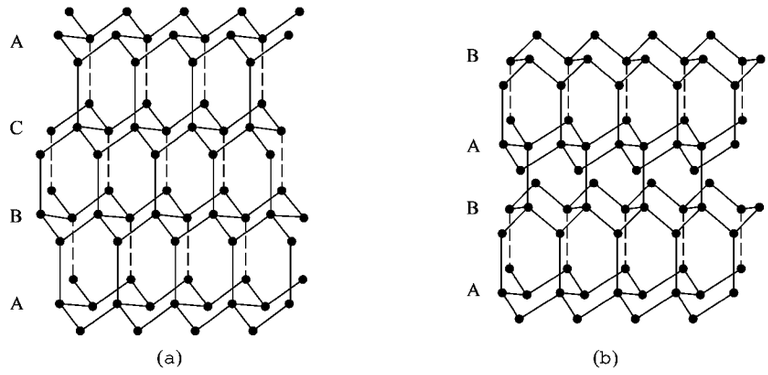

Fig. 1. Crystal structures of (**a**) cubic diamond and (**b**) lonsdaleite. A, B, and C indicate the stacking sequence of sheets of atoms.

Besides the single crystals usually implied in a discussion of diamond, it also occurs in nature in the form of polycrystalline aggregates. These can be classified into two types based on origin: carbonado and ballas. The former is an aggregate of previously formed grains that have become cemented to each other to varying degrees of bonding. Some varieties such as framesite show evidence of mechanical deformation during the aggregation process. Similar twinning structures are found in synthesized compacts. Ballas refers to a polycrystalline aggregate of diamond grains that were growing simultaneously as opposed to an assemblage of previously grown crystals. Specifically the term refers to a ball-shaped polycrystalline diamond often with a radial structure like some hailstones. Contrary to carbonado, ballas is quite free of second phases, and the grain boundaries are almost crystallographic in nature. Most synthesized compacts have a structure that resembles carbonado rather than ballas. Bort is a general term used to describe low-grade industrial diamond suitable only for use in a fragmented form.

Chemical Composition. Diamond is nominally pure carbon with a ^{12}C:^{13}C ratio of about 99:1. Although other elements are often reported in analyses, most are considered to be present in oxide, silicate, and sulfide phases as inclusions in the diamond. Only boron, nitrogen, and possibly beryllium are considered to be truly substitutional in the lattice. Hydrogen and oxygen, possibly as OH, may also be important structural contaminants though they may also be present as second-phase gases along with CO, CO_2, H_2O, CH_4, and other species (20).

The concentration of B in natural IIb diamonds is about 0.25 ppm and as much as 270 ppm in synthesized crystals; a crystal with about 10 ppm B is essentially deep blue. Dissolved nitrogen can range up to 2500 ppm atomic in Type Ia natural stones and to about 500 ppm atomic for synthesized Type Ib. References 9, 14–19 provide qualifications on these data.

The classification of diamond into four principal types is based on the presence of nitrogen and boron and their effect on the ir and uv transmission (14–19,21). Nominally pure carbon is Type IIa, which has the highest thermal conductivity and is transparent out to 10.6 μm. Type IIb (boron-doped *p*-type semiconductor) is blue, eg, the Hope diamond. Most natural diamonds are Type Ia, which is characterized by the presence of platelets, made visible by transmission electron microscopy on the (100) planes. The exact nature of these platelets is still controversial, but they are often called nitrogen platelets (possibly N–N or C–N clusters). An increase in the high temperature bending strength of Type Ia over IIa diamonds has been attributed to the platelets interfering with dislocation motion (22). When the nitrogen is in this form, the crystals can be essentially colorless, in contrast to the yellow Type Ib, which has nitrogen in substitutional positions in the lattice. Most synthesized diamond is Ib unless special precautions are taken to remove nitrogen. Type Ib can be converted to a Type Ia and vice versa by annealing at high pressures and temperatures (23,24). This was first established in the laboratory and is now presumed to be the way nature made what is essentially a two-phase material, Type Ia. If this conversion could be carried out in a practical manner, it would be of some interest in improving the value of slightly yellow gemstones.

The main silicate inclusions in natural diamond are pyroxenes and garnet *[12178-41-5]*, and the understanding of the conditions of their formation from laboratory studies is the basis for the determination of the P–T conditions when diamond was formed (2–6). CO, CO_2, H_2, H_2O are also found in diamond (20), and it is possible that diamond nucleated and grew in a liquid in a C–H–O system, perhaps immiscible, but in equilibrium with the silicate matrix (4). Graphite *[7440-44-0]* is also a common inclusion in natural diamond.

Diamond is thermodynamically unstable at ambient conditions, but unless heated to 650°C in air (oxidation to CO_2) or 1700°C in vacuum or an inert atmosphere (graphitization), it will remain as diamond indefinitely. To convert graphite directly to diamond requires very high pressures, about 12 GPa (120 kbar) and temperatures about 1800°C (see Fig. 1 in CARBON, DIAMOND SYNTHETIC). For synthesis of industrial diamond these conditions can be lowered by the presence of metal solvent catalysts. More recent work on the thermodynamically stable region for diamond indicates a positive slope for the melting curve instead of the negative slope deduced previously on the basis of analogy to the P–T diagrams for Si and Ge (25). This has important implications for the origin and extent of diamond in the earth. A "... diamond as big as the Ritz ..." may indeed exist at great depths in the earth (26).

Diamond is chemically inert to inorganic acids, but can be etched in oxidizing molten salts such as KNO_3 at 600°C. Carbon as diamond or graphite is soluble in several metals, particularly Fe, Ni, Co, and other Group (VIII) elements. This imposes a serious limitation on the use of diamond for machining alloys based on these materials in spite of the high hardness of diamond. At the temperatures developed at a cutting tool tip, diamond reacts with these metals. However, the same reactions are the basis for the bonding of diamond in metals for tools because of the wetting of diamond by carbide-forming metals (27,28).

Hardness. Diamond is the hardest material known because of its combination of a three-dimensional arrangement of tetrahedrally coordinated C–C bonds with a bond distance of 0.154 nm. The Knoop hardness (*K*) is in the range of 68.7–98.1 kN m^2 (7,000 to 10,000 kgf mm^2). Harder materials have been postulated on the basis of bond distance, but so far they have not been found or made in a useful form (29,30). Diamond is twice as hard as cubic BN ($K = \sim 44$ kN m^2), which in turn is twice as hard as SiC ($K \sim 23.5$ kN m^2). The hardness of diamond varies as a function of orientation; this is important when mounting stones for drill bits or in polishing gemstones. The table, the largest facet of a brilliant cut diamond, is generally the (100) face because it is easier to saw and polish than the (111) face using traditional techniques. The use of lasers to cut diamonds diminishes the importance of orientation dependence of hardness (qv) in some industrial operations.

Cleavage. Although hard, diamond is also very brittle and cleaves readily on the (111) plane and also on other planes under certain conditions. The ability to fracture is useful in cutting and grinding applications because the crystals are self-sharpening. For other procedures such as sawing rocks or concrete, tougher stones are desirable. The uncontrolled fracture of a gemstone is disastrous, but some of the famous large gem stones were first reduced to desired sizes by controlled cleavage to avoid the time-consuming process of sawing (7,31–33).

Mechanical Properties. Measurement of the mechanical properties of diamond is complicated, and references should be consulted for the various qualifications (7,34). Table 1 compares the theoretical and experimental bulk modulus of diamond to that for cubic BN and for SiC (29) and compares the compressive strength of diamond to that for cemented WC, and the values for the modulus of elasticity *E* to those for cemented WC and cubic BN.

Table 1. Mechanical Properties of Diamond and Other Hard Materials, GPa[a]

	Diamond	Cubic BN	WC[b]	SiC

bulk modulus	440	370		211
compressive strength	8.69		4–6	
modulus of elasticity, *E*	950–1100	890	460–675	

[a] To convert GPa to psi, multiply by 145,000.

[b] Cemented.

Thermal Conductivity. The value of 2000 W (m·K) at room temperature for Type IIa natural stones is about five times that of Cu, and recent data on 99.9% isotopically pure ^{12}C Type IIa synthesized crystals are in the range of 3300–3500 W (m·K) (35). This property combined with the high electrical resistance makes diamond an attractive material for heat sinks for electronic devices.

Thermal Expansion. The averaged value of the coefficient of linear thermal expansion of diamond over the range 20 to 100°C is 1.34×10^{-6} cm cm °C and 3.14×10^{-6} from 20 to 800°C. At room temperature the values for silica glass and diamond are 0.5×10^{-6} and 0.8×10^{-6}, respectively. The relatively low expansion combined with the low reactivity of diamonds, except for carbide formation, leads to some challenges in making strong bonds between diamond and other materials.

Optical Properties. The high refractive index (2.42 at 589.3 nm) and dispersion (0.044) are the basis for the brilliance and fire of a properly cut gemstone. The optical transmission out to 10.6 μm for Type IIa diamonds makes possible windows for CO_2 lasers and for devices such as were in the Venus probe. References should be consulted for the details of the optical transparency of the different type diamonds (9,14,16–19). The direct band gap for diamond is 5.47 *e*V. Natural diamond exhibits many colors, and color modification by irradiation and annealing is common (36). Though cubic, most natural diamonds show strain birefringence under crossed polaroids.

Electrical and Electronic. Diamond is an electrical insulator ($\sim 10^{16}$ Ω cm) unless doped with boron when it becomes a *p*-type semiconductor with a resistivity in the range of 10^{-1} to 100 Ω cm. *n*-Type doping has often been claimed but is less certainly established. The dielectric constant of diamond is 5.58.

Applications

Industrial Abrasive Grain. These applications of diamond are based on its high hardness, wear resistance, ability to self-sharpen as it cleaves, thermal conductivity, and chemical inertness. Loose abrasive grain is used in lapping and polishing operations, eg, on the scaife used for facetting gem crystals and polishing rock materials for monuments and buildings. Single-point tools for engraving, truing, or cutting applications are made by mounting an individual stone in metal holders (27,28,37). Other uses for single stones are as phonograph needles, bearings, surgical knives, and wire dies. The differential hardness of diamond is the cause of the nonuniform wear, or loss of roundness, of a wire die. If sintered (polycrystalline) diamond is used for wire dies, the anisotropic wear problem disappears.

For many applications such as grinding, cutting, drilling, and sawing, abrasive grains are mounted in resin, metallic, or vitreous bonding materials on wheels, disks, or saw blade sectors. Metallic bonding can be accomplished by electroplating as well. The grooving of concrete runways and roads is a well-known example of the use of impregnated diamond saw blades. An interesting new development is as beads, which are strung on long wires for sawing blocks of stone from quarries.

In 1988, 14,230 kg (71,147,000 carats) of natural grit and stones at a total value of $130,300,000 were imported into the United States. The average per carat value of the grit and stones was $0.82 and $9.31, respectively (38). However, about 90% of industrial diamond is now synthesized.

Electronic. Diamonds have been used as thermistors and radiation detectors, but inhomogeneities within the crystals have seriously limited these applications where diamond is an active device. This situation is rapidly changing with the availability of more perfect stones of controlled chemistry from modern synthesis methods. The defect structure also affects thermal conductivity, but cost and size are more serious limitations on the use of diamond as a heat sink material for electronic devices.

Optical. Besides the gem qualities dependent on optical properties, diamond is very useful as a light-transmitting window for lasers and for simple windows for monitoring chemical processes in corrosive and otherwise hostile environments.

Gemstones. From standards set by the gem trade a small amount of yellow lowers the value of a gemstone, but when the color is strong and uniformily distributed, the value increases in what is called the fancy class. Pink diamonds are very rare and highly prized. Most of the demand is for colorless stones, of which only a small percentage are totally free of flaws. The selection of stones and the cutting to maximize the final value is a mix of science and art based on experience. For the procedures for transforming a natural stone to a gem see reference 33. Besides the traditional cutting centers such as in Belgium and Israel, India has recently become a primary supplier of the smaller sizes of cut stones via a cottage industry. In 1989, De Beers sales of uncut diamonds was about five billion dollars, and the retail value of the U.S. diamond jewelry market was nearly $12 billion. The supply and price of diamond for jewelry is rigidly controlled (31,39).

Research. A significant impact on research at high pressure has come about with the use of gem quality diamonds as Bridgman-type anvils in a small compact high pressure device (40–42). With this type of apparatus, pressures greater than those at the center of the earth (360 GPa 3.6 Mbars) have been reached, and phase transformations of many materials have been studied. Because of the x-ray transparency of diamond, it is possible to determine the structure of the phases under pressure. Because of the strenuous environment, crystals selected for this application have to be of very high quality.

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DIAMOND, SYNTHETIC

Interest in the synthesis of diamond *[7782-40-3]* was first stimulated by Lavoisier's discovery that diamond was simply carbon; it was also observed that diamond, when heated at 1500–2000°C, converted into graphite *[7782-42-5]*. In 1880, the British scientist Hannay reported (1) that he made diamond from hydrocarbons, bone oil, and lithium, but no one has been able to repeat this feat (2). About the same time, Moissan believed (3) that he made diamond from hot molten mixtures of iron and carbon, but his experiments could not be repeated (4,5).

The graphite–diamond equilibrium line up to 1200 K was calculated in 1938 (6) by using the observed heat, compressibility, and thermal expansion data of the two components (Fig. 1). Subsequently, estimates of the diamond–graphite equilibrium line were refined and extended (9) and the extrapolation to higher temperatures fits the experimental data (10). It is evident that diamond is not thermodynamically stable below a pressure of about 1.6 GPa (16 kbar) and early investigators were using pressures in their experiments where diamond would have been unstable.

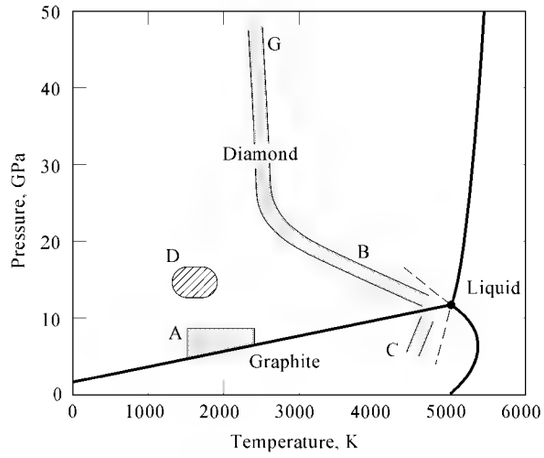


Fig. 1. Carbon-phase diagram where A, solvent-catalyzed diamond growth; B–G, diamond formation directly from graphite; C, graphite formation from diamond, D, approximate region where formation of Lonsdaleite occurs from well-ordered graphite crystals (7,8). To convert GPa to atm, multiply by 10,000.

Reproducible Laboratory Diamond Synthesis

In 1955, a team of research workers at General Electric developed the necessary high pressure equipment and discovered solvent–catalytic processes by which ordinary forms of carbon could be changed into diamond.

In the attempt at diamond synthesis (4), much unsuccessful effort was devoted to processes that deposited carbon at low, graphite-stable pressures. Many chemical reactions liberating free carbon were studied at pressures then available. New high pressure apparatus was painstakingly built, tested, analyzed, rebuilt, and sometimes discarded. It was generally believed that diamond would be more likely to form at thermodynamically stable pressures. The refractory nature of carbon indicated that temperatures of about 2000 K and pressures of 5–10 GPa (50–100 kbar) might suffice. Months after operating pressures of ca 7 GPa (70 kbar) had been attained, a reproducible diamond synthesis called the catalyzed diamond synthesis was finally achieved.

Catalyzed Synthesis

In this process, a mixture of carbon (eg, graphite) and catalyst metal is heated high enough to be melted while the system is at a pressure high enough for diamond to be stable. Graphite is then dissolved by the metal and diamond is produced from it. Effective catalysts are Cr, Mn, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, and Ta, and their alloys and compounds. If the metal is not molten, graphite is obtained instead of diamond even at pressures high enough to produce diamond. The exception is tantalum, which does not have to be molten to be effective.

Generally the two requirements that the catalyst be molten and diamond be stable define a pressure–temperature area in which diamond may form with the aid of a particular catalyst system. This diamond-forming region is illustrated in Figure 2 for the nickel–carbon system. The shaded area in which diamond may form is bounded along the temperature axis by the nickel–carbon eutectic melting line and along the pressure axis by the graphite–diamond equilibrium line. Other catalyst metal systems define similarly shaped regions above the graphite–diamond equilibrium line. The region for platinum, for example, lies at higher pressures and temperatures than that of nickel because of the higher melting temperature of the Pt–C eutectic. Diamonds have been grown at temperatures as low as ca 1500 K and at a pressure of ca 5 GPa (50 kbar), using certain alloys of iron, nickel, and chromium as catalysts; the growth rate then is rather slow and the diamonds are heavily contaminated with metal, carbides, and graphite. Observation of the growth or disappearance of diamond has permitted a closer estimate of the course of the equilibrium line between graphite and diamond as indicated by the dashed line in Figure 2 extending toward 3000 K.

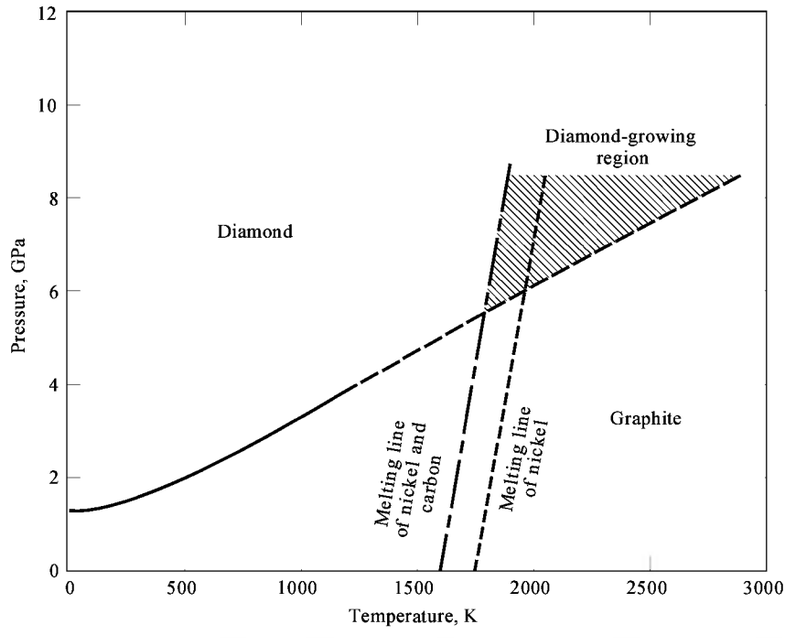


Fig. 2. Diamond-forming region for the nickel–carbon system (3). To convert GPa to kbar, multiply by 10.

Apparatus. Many kinds of apparatus have been devised for simultaneously producing the high pressures and temperatures necessary for diamond synthesis (11). An early, successful design is the belt apparatus (12), shown in Figure 3. In this apparatus, two opposed, conical punches, made of cemented tungsten carbide and carried in strong steel binding rings, are driven into the ends of a short, tapered chamber that is also made of cemented tungsten carbide supported by strong steel rings. A compressible gasket, constructed in a sandwich-fashion of stone, usually pyrophyllite, and steel cones, seals the annular gap between punch and chamber, distributes stress, provides lateral support for the punch, and permits axial movement of the punches to compress the chamber contents. The reaction zone, usually a cylinder, is buried in pyrophyllite stone in the chamber. The pyrophyllite, a good thermal and electrical insulator, is easily machined and transmits pressure fairly well. The reaction zone is heated electrically with a heavy current.

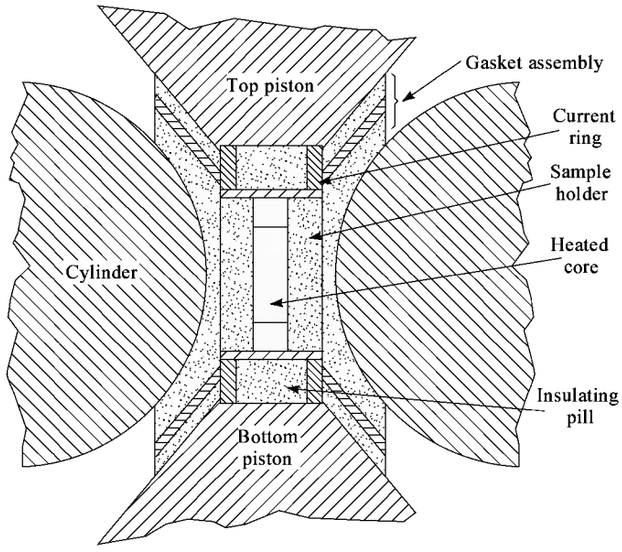


Fig. 3. Cross section of belt high pressure apparatus.

The reaction zone temperature is measured by introducing thermocouple wires through the compressible gaskets, whereas the pressure is estimated by a calibration technique. A relationship is obtained between the force on the pistons and the pressure in the chamber by loading the reaction zone with certain metals in which abrupt changes of electrical resistance occur at certain pressures and by noting the piston forces at which these changes occur. Typical pressure changes used are those occurring in bismuth at 2.5 and 7.5 GPa (25 and 75 kbar), in thallium at 3.7 GPa (37 kbar), and in barium at 5.3 GPa (53 kbar); such resistance changes usually coincide with changes of phase or structure in the metals at high pressure.

A belt apparatus is capable of holding pressures of 7 GPa (70 kbar) and temperatures of up to 3300 K for periods of hours. The maximum steady-state temperatures are limited by melting of the refractory near the reaction zone (13).

Figure 4 shows an arrangement of carbon and catalyst metal. As the sample is heated at high pressure, the metal next to the graphite usually melts and diamond begins to form there. An exceedingly thin film of molten metal (at most a few thousandths of a cm thick) separates the newly formed diamond from the unchanged graphite. This film advances like a wave through the mass of graphite and transforms it to diamond. The speed at which this film travels depends only slightly on the temperature but increases very rapidly to at least 1 mm s as the pressure is increased above that necessary for diamond to be stable. Thus all graphite present in the sample, with the exception of carbon dissolved in the metal, may be transformed to diamond in time intervals of a few minutes to a few hours, depending on the pressure, temperature, and catalyst system. A mass of diamond crystals in a metallic matrix remains (Fig. 5), where most of them are still covered by the catalyst metal film, which is dissolved in acids to free the diamonds.

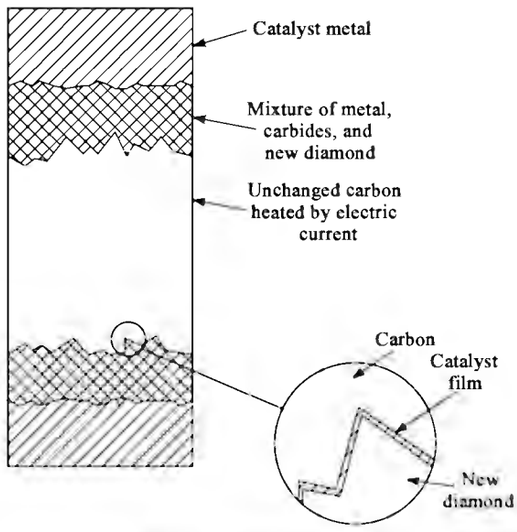


Fig. 4. Diamond synthesis cell.

Fig. 5. Mass of freshly formed diamonds.

Comprehensive accounts of the methods and phenomena involved in diamond synthesis can be found in references 14–16.

Crystal Morphology. Size, shape, color, and impurities are dependent on the conditions of synthesis (14–17). Lower temperatures favor dark colored, less pure crystals; higher temperatures promote paler, purer crystals. Low pressures (5 GPa) and temperatures favor the development of cube faces, whereas higher pressures and temperatures produce octahedral faces. Nucleation and growth rates increase rapidly as the process pressure is raised above the diamond–graphite equilibrium pressure.

The growing faces of diamond crystals are chemically active and tend to adsorb and incorporate certain impurities, particularly those that may be accommodated in the diamond without greatly straining the host lattice. Common contaminants are graphite, nitrogen, and certain catalyst metals, particularly nickel. The lattice dimensions of nickel and diamond are similar enough so that invisible clusters of nickel, at least several thousand atoms in diameter, may be included in diamond in an oriented sense. X-ray diffraction studies (14) show that these crystallites are oriented parallel to the diamond host lattice; the composite crystals, usually containing less than 1% of nickel, are ferromagnetic with approximately the same Curie temperature as massive nickel. It appears that even though synthetic diamonds are essentially the same as natural diamonds, there are enough differences between them, mainly in structure and impurity content, to permit an observer to distinguish between them.

Crystal Growth. If diamond seed crystals are placed in the active diamond growing zone of a typical graphite–catalyst metal apparatus, new diamond usually forms on the seed crystals. However, the new growth tends to be uneven in thickness and quality, with gaps or inclusions of foreign material. Such defects probably appear because the main driving force for the nucleation and growth under these conditions is the Gibbs free energy difference between diamond and graphite, which is a function of pressure, temperature, and composition; none of these variables can be sufficiently controlled. However, excellent growth can be obtained if pressure and composition are held relatively constant while the change of composition with temperature is employed as a driving force. In practice, small diamonds are used as the source of carbon in a hotter portion of a molten catalyst metal bath at about 1500°C and 5.5 GPa (55 kbar). Diamond seed crystals are placed in a cooler portion of the bath and the difference in solubility resulting from the difference in temperature causes diamond to recrystallize on the seed crystals in a slow, controlled fashion (18). Growth periods up to a week are used for the larger crystals of about 5 mm or 1 carat (0.2 g). The process is barely commercially feasible, but the control of growth conditions and bath compositions permits the formation of various types of high quality diamond crystals for property studies (19,20). A few parts per million of boron impart a blue color and make the diamonds semiconducting (see SEMICONDUCTORS). A few dozen parts per million of nitrogen give a yellow color. Colorless crystals of outstanding purity, crystal perfection, and thermal conductivity have been made (21–23), especially when pure ^{12}C is used as a carbon source (Fig. 6) (24).

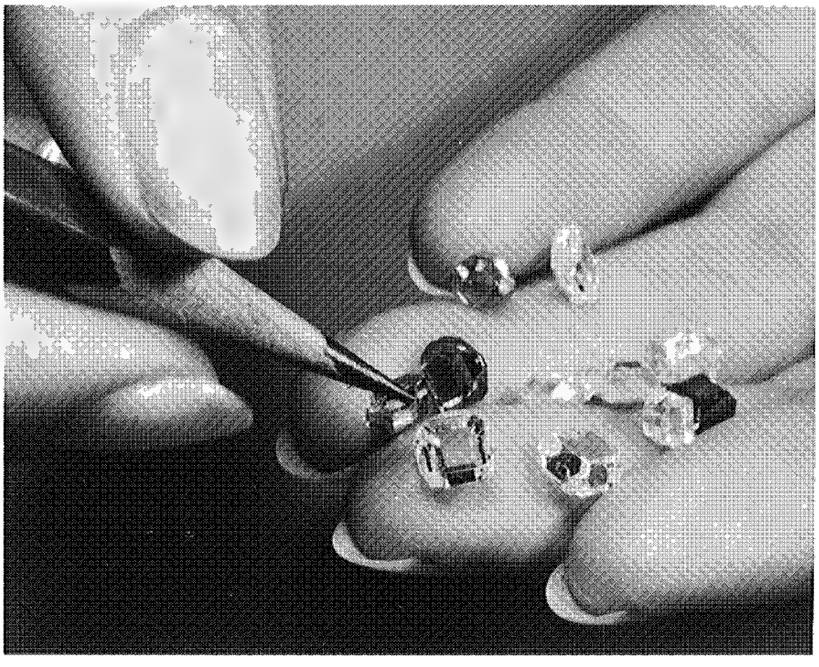


Fig. 6. Synthesized high quality single-crystal diamonds.

Direct Graphite-to-Diamond Process

In this process, diamond forms from graphite without a catalyst. The refractory nature of carbon demands a fairly high temperature (2500–3000 K) for sufficient atomic mobility for the transformation, and the high temperature in turn demands a high pressure (above 12 GPa; 120 kbar) for diamond stability. The combination of high temperature and pressure may be achieved statically or dynamically. During the course of experimentation on this process a new form of diamond with a hexagonal (wurtzitic) structure was discovered (25).

Shock Synthesis. When graphite is strongly compressed and heated by the shock produced by an explosive charge, some (up to 10% o) diamond may form (26,27). These crystallite diamonds are small (on the order of 1 μm) and appear as a black powder. The peak pressures and temperatures, which are maintained for a few microseconds, are estimated to be about 30 GPa (300 kbar) and 1000 K. It is believed that the diamonds found in certain meteorites were produced by similar shock compression processes that occurred upon impact (5).

Some diamond powder is produced commercially by shock-wave methods. The DuPont process (28) exposes small, well-crystallized graphite lumps in nodular cast iron to the brief, intense pressure generated by a suitable charge of high explosive. The graphite lumps are more compressible and reach much higher temperatures than the surrounding iron at the peak pressures, which last for a few microseconds, and part of the graphite turns into diamond. The carbon is cooled rapidly by the iron environment and the new diamond is thereby preserved. After recovery of the mass, the iron is dissolved and the diamond is separated by controlled oxidation of the graphite. The final product is a gray powder with particles ranging in size up to 30 μm.

The annual production of diamond by this process is only a small fraction of total industrial diamond consumption.

Static Pressure Synthesis. Diamond can form directly from graphite at pressures of about 13 GPa (130 kbar) and higher at temperatures of about 3300–4300 K (7). No catalyst is needed. The transformation is carried out in a static high pressure apparatus in which the sample is heated by the discharge current from a capacitor. Diamond forms in a few milliseconds and is recovered in the form of polycrystalline lumps. From this work, and studies of graphite vaporization melting, the triple point of diamond, graphite, and molten carbon is estimated to lie at 13 GPa and 5000 K (Fig. 1) (7,8,15).

At pressures of 13 GPa many carbonaceous materials decompose when heated and the carbon eventually turns into diamond. The molecular structure of the starting material strongly affects this process. Thus condensed aromatic molecules, such as naphthalene or anthracene, first form graphite even though diamond is the stable form. On the other hand, aliphatic substances such as camphor, paraffin wax, or polyethylene lose hydrogen and condense to diamond via soft, white, solid intermediates with a rudimentary diamond structure (29).

Crystal Structure. Diamonds prepared by the direct conversion of well-crystallized graphite, at pressures of about 13 GPa (130 kbar), show certain unusual reflections in the x-ray diffraction patterns (25). They could be explained by assuming a hexagonal diamond structure (related to wurtzite) with $a = 0.252$ and $c = 0.412$ nm, space group $P6_3/mmc$ D_{6h}^4 with four atoms per unit cell. The calculated density would be 3.51 g/cm^3, the same as for ordinary cubic diamond, and the distances between nearest neighbor carbon atoms would be the same in both hexagonal and cubic diamond, 0.154 nm.

Figure 7 shows the crystal structures of graphite, ordinary (cubic) diamond, and hexagonal diamond. The layers of carbon atoms lie in flat sheets in graphite, but in diamond the sheets are more wrinkled and lie closer together. Taken separately, the sheets are similar, but they may be stacked in various lateral positions and still have bonding between them.

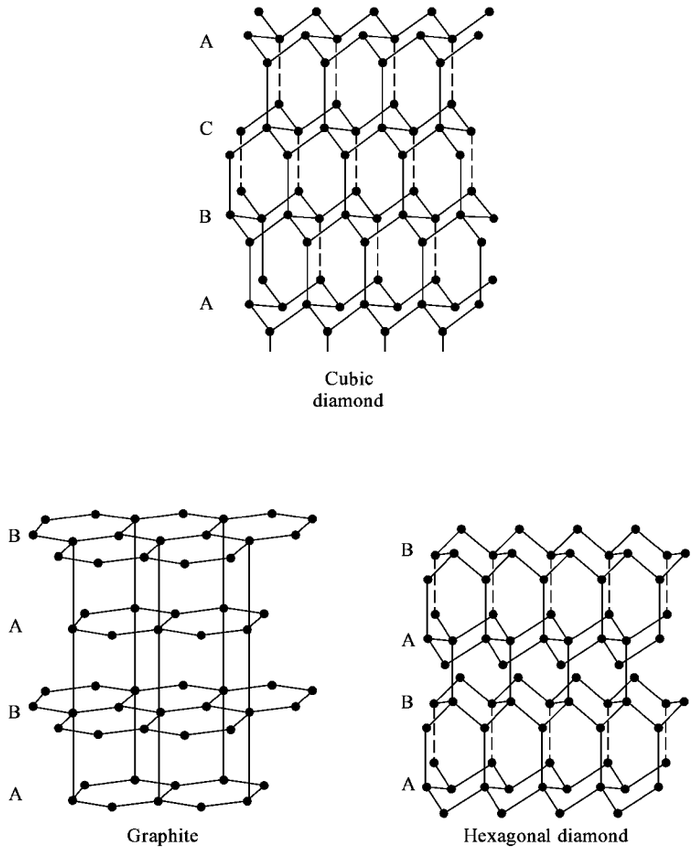


Fig. 7. Crystal structures of graphite, ordinary cubic diamond, and hexagonal diamond; A, B, and C are the lateral positions.

In ordinary diamond (zinc-blende structure) the wrinkled sheets lie in the (111) or octahedral face planes of the crystal and are stacked in an ABCABC sequence. In real crystals, this ABCABC sequence continues indefinitely, but deviations do occur. For example, two crystals may grow face-to-face as mirror images; the mirror is called a twinning plane and the sequence of sheets crossing the mirror runs ABCABCCBACBA. Many unusual sequences may exist in real crystals, but they are not easy to study.

In hexagonal diamond (wurtzite structure) the wrinkled sheets are stacked in an ABABAB sequence, as shown in the Figure 7. Looking down on the stack from above, hexagonal holes can be seen formed by the six-membered carbon rings. The crystal has hexagonal symmetry about this axis, hence the name hexagonal diamond, or wurtzitic carbon.

The sequence of sheets in graphite is also ABAB; however, an examination of the atomic positions shows that they are not simply related to those in either kind of diamond. Thus the simple compression of graphite should not be expected to yield diamond. However, well-crystallized graphite, in which the ABAB sequence extends for at least hundreds of layers, tends to form wurtzitic carbon. The rare rhombohedral form of graphite has an ABCABC sequence of sheets, but its scarcity has hindered its study as a source for diamond.

Some reshuffling of atoms is necessary to complete the transformation of graphite into wurtzitic carbon crystals of a size large enough to detect. The necessary atomic mobility can be provided by heating to about 1500 K (area D in Fig. 1). Various departures from ideality make it difficult to prepare pure wurtzitic carbon, even when the best graphite is used. The products obtained so far always contain some ordinary diamond as well as remnant graphite, parts of which are compressed by the nearby diamond regions. Hence, many physical properties of wurtzitic carbon are not well-known. It has been found in the Canyon Diablo meteorite and in some shock-made diamond from DuPont, but not in regular synthetic industrial diamond. This form of carbon has been given the name lonsdaleite.

Metastable Vapor-Phase Deposition

Metastable growth of diamond takes place from gases rich in carbon and hydrogen at low pressures where diamond would appear to be thermodynamically unstable. The subject has a long history, beginning with work in the United States and Russia as early as 1962 (30–32) but not achieving widespread interest and acceptance until about 1986 after successful work in Japan.

In a typical use of this method, a mixture of hydrogen and methane is fed into a reaction chamber at a pressure of about 1.33 kPa (10 torr). The substrate upon which diamond forms is at about 950°C and lies about 1 cm away from a tungsten wire at 2200°C. Small diamond crystals, 1 mm or so in size, nucleate and grow profusely on the substrate at a rate around 0.01 mm h to form a dark, rough polycrystalline layer with exposed octahedral or cubic faces, depending on the substrate temperature.

The carbon-bearing gas can be a saturated or unsaturated hydrocarbon, an alcohol, ketone, etc. At the high gas temperature near the tungsten filament the predominant stable carbon species is acetylene and a significant fraction, eg, 7% of the hydrogen is dissociated into hydrogen atoms. Suitable concentrations of active species can also be produced in a plasma discharge. The species move through the other gases to the growing diamond surface where the hydrogen atoms, if sufficiently numerous, combine with existing and arriving carbon atoms to put them into the tetrahedral bonding state of diamond on the growing surface. Pure diamond would be thermodynamically unstable at 950°C and 1.33 kPa (10 torr), but evidently diamond surface covered with hydrogen is stable in the presence of enough gaseous carbon species to suppress methane formation. If the surface temperature is below 500°C, surface reactivity drops and nondiamond carbon forms. If the surface temperature is above 1100°C, graphitic carbon or methane forms instead of diamond (33,34).

Although the apparatus and process are relatively simple, the energy costs to maintain the required temperatures are significant. Also, the diamonds formed are not suitable for all industrial uses. Thus the process as presently developed is regarded as an adjunct to high pressure commercial diamond synthesis. In principle, unusually large shapes, such as large area films, free-standing membranes, or coated tools, might be grown. However, success in these directions is currently limited by the thermal expansion differences between substrate and diamond and by the free-surface roughness of the deposited diamond (35).

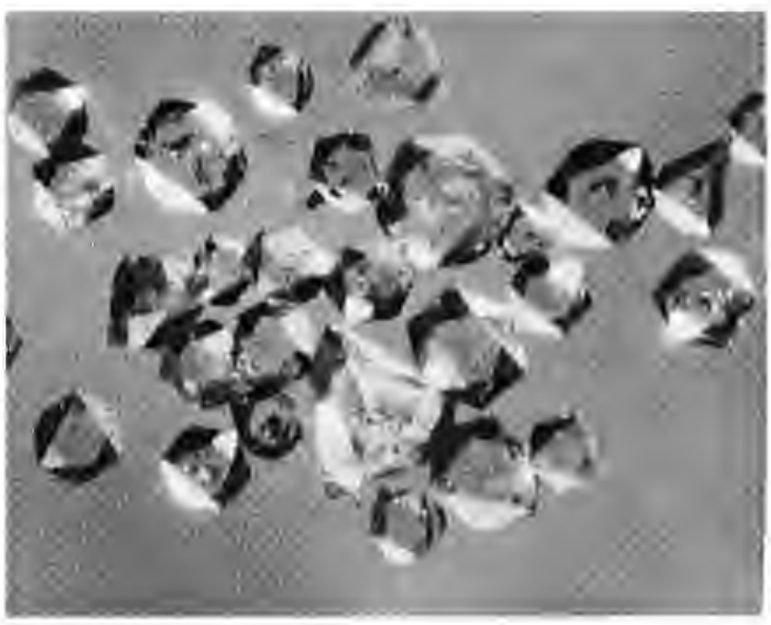
By beginning with ^{12}C methane, the diamonds formed have only ^{12}C in them. These tiny diamonds may then be used as the carbon source to form large (5 mm) single crystals by growth from molten catalyst metal in a temperature gradient. The resulting nearly pure crystals have outstanding thermal conductivities suitable for special applications as windows and heat sinks (24).

The Synthetic Diamond Industry

Soon after the first successful diamond synthesis by the solvent–catalyst process, a pilot plant for producing synthetic diamond was established, the efficiency of the operation was increased, production costs declined, and product performance was improved while the uses of diamond were extended. Today the price of synthesized diamond is competitive with that of natural diamonds.

Several kinds of diamonds can be produced, depending on synthesis conditions, with each kind especially suited for particular uses. For example, the shaping of cemented tungsten carbide is an operation that consumes a large fraction of industrial diamond grit, and friable crystals with many sharp edges and corners, such as shown in Figure 8**a**, mounted in a free-cutting resinoid or vitrified wheel matrix, are the most suitable for this task. The excellent abrasive properties seem to be caused by a better bond between diamonds and wheel matrix and a greater number of constantly renewed sharp cutting edges per abrasive grain.

(a)



(b)

Fig. 8. (**a**) Synthetic diamond grit for resinoid or vitreous bond (free-cutting) abrasive wheels, and (**b**) synthetic diamond grit for metal bond abrasive wheels.

When the diamond grit is carried in a sintered metal matrix in the abrasive tool, tougher, more coherent, block-shaped crystals, as shown in Figure 8**b**, are preferred. The combination of more severe operating conditions and the strong metallic matrix imposes high loads upon each abrasive grain and the grains must be strong enough to resist these high cutting forces without crumbling (see ABRASIVES).

The bulk of synthetic industrial diamond production consists of the smaller crystal sizes up to 0.7-mm particle size (25 mesh). This size range has wide utility in industry, and a significant fraction of the world's need for diamond abrasive grit is now met by synthetic production yielding thousands of kilograms per year. Because the raw materials are plentiful, synthetic production could, if necessary, supply the world demand for diamond abrasive. Development work continues in order to improve size and utility of the manufactured product and to realize the full potential of diamonds at minimum cost. An appreciable increase in performance has been obtained by coating the diamonds with a thin layer of nickel or copper, before incorporating them into wheels. The thin layer of metal apparently improves adhesion and heat transfer.

Semiconducting Diamonds. With the exception of the rare, natural Type IIb, diamond is normally a good electric insulator. However, semiconducting diamonds are prepared by adding small amounts of boron, beryllium, or aluminum to the growing mixture, or by diffusing boron into the crystals at high pressures and temperatures. Such diamonds are *p*-type, with activation energies for conduction usually ranging between 0.1 and 0.35 eV. Addition of boron gives the diamonds a blue color. Some of these crystals have been used as thermistors with a very wide, stable operating temperature

range, 200 to 500°C, and having nominal resistance of 4,000–40,000 ohms (35).

Sintered Diamond Masses. Some natural diamonds known as carbonado or ballas occur as tough, polycrystalline masses (see CARBON, DIAMOND, NATURAL). The production of synthetic sintered diamond masses of comparable excellent mechanical properties has only been achieved recently (36). The essential feature is the presence of direct diamond-to-diamond bonding without dependence on any intermediate bonding material between the diamond grains, since no extraneous bonding material can match the stiffness, thermal conductivity, and hardness of diamond. Formidable inherent obstacles are encountered when the sintering of small diamond grains is sought (16,37) and the process must be run at high pressures to preserve the diamonds from graphitization.

Since these masses of polycrystalline diamond possess extensive diamond-to-diamond bonding, they have, in contrast to single-crystal diamond, excellent crack resistance, since any crack that begins in one crystal on an easy cracking plane (parallel to an octahedral face) is halted by neighboring crystals that are unfavorably oriented for their propagation.

Natural single-crystal diamond and carbonado can now be replaced in many industrial uses by sintered diamond tool blanks. Such tool blanks are available in disks and cores. The disks, or sectors of disks, consist of a thin (0.5–1.5 mm) layer of sintered diamond up to about 50 mm diameter on a cemented tungsten carbide-base block about 3–6 mm thick. Using diamond abrasive, such blanks can be formed into cutting tools of various shapes. Typical tool blanks are shown in Figure 9. The wire dies have diamond cores up to 10 mm in diameter and 10 mm in length, which are encased in a cemented tungsten carbide sleeve up to 25 mm in diameter.

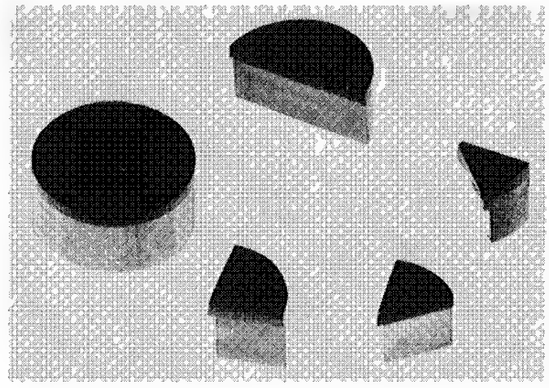


Fig. 9. Sintered polycrystalline diamond cutting tool blanks.

The disks enjoy wide usage as cutting or shaping tools for a variety of hard, abrasive materials such as fiber-reinforced composites, ceramics, rock, silicon-rich aluminum alloys (37). Their toughness, shock resistance, ready availability, and uniform reliable properties have greatly enlarged the use, scope, and durability of diamond cutting tools over that of natural single crystals. They are not suitable for use on ferrous or nickel-base alloys because of the reactivity of diamond with these metals when hot. For such metals, sintered cubic boron nitride tools are useful (see BORON COMPOUNDS). They show considerable promise as well-drilling bits. The diamond core pieces are commonly pierced and used as wire-drawing dies (38). The uniform polycrystalline character and resistance to bursting of such dies give them improved performance and utility as compared to single-crystal diamond dies, and the larger sizes cost less. Some of them have drawn over 160,000 km of copper wire before repolishing was needed.

A few special high pressure pistons with sintered diamond working faces have been made for laboratory experiments. Although the sample volume is very small, pressures of 50 GPa (500 kbar) at temperatures of up to 500°C have been reached with such an apparatus (39).

C_{60} Conversion. Buckminsterfullerene can be crushed to diamond by high pressure applied at room temperature (40). The process is highly efficient and fast at room temperature, suggesting industrial potential.

Economic Aspects

About 90% of industrial diamond is synthesized at high pressures because its price is relatively low, and it can be tailor-made for efficiency in each application. Industrial diamond grit is currently priced at $5 to $25 per gram. The cheapest material is powder with particle sizes of a few micrometers, because this material is the easiest to make and also is an inevitable by-product of attrition during the sizing and sifting operations used to classify larger crystals for various purposes. The most expensive grit materials are the large, tough, blocky crystals in the 0.3–1 mm size range used for sawing rock and concrete. The main manufacturing expense is not raw materials but maintenance of the special high pressure apparatus. The small crystals made by metastable vapor deposition from methane have slightly higher prices, limited mainly by electric power costs, but are not yet widely sold. Sintered diamond tools fetch a much higher price, several hundred dollars per gram (five carats), of diamond, because of the expenses of sintering and shaping them. Pieces of large (2–6 mm) single crystals for special applications are available from Sumitomo Electric of Japan for a few hundred dollars per carat (0.2 g) but are only a tiny part of the industrial market.

Total worldwide sales of industrial diamond are currently about one billion dollars (ca 100 t) per year. They are made in 16 countries; the largest producers are General Electric, De Beers, which also has a large stake in natural diamonds, several Japanese firms, the People's Republic of China, and Russia. The market is very competitive, and manufacturers are reluctant to disclose detailed sales information.

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NATURAL GRAPHITE

Natural graphite, the mineral form of graphitic carbon, occurs worldwide. It differs from the carbon of coal and of diamond in its predominantly lamellar hexagonal crystal structure. The ore usually contains associated silicate minerals that vary in kind and amount with the source. Except for technical terminology, the name natural graphite is seldom used. It may be simply termed graphite or any of several common names such as plumbago, black lead, silver lead, carburet of iron, and reissblei. The macrophysical form depends on geological genesis, whereas the properties depend on both the macrophysical form and associated mineral suite. The commercial value depends on specific characteristics such as form, percentage and kind of mineral suite, and availability. Graphite occurs in widely distributed places as flakes, lumps, and cryptocrystalline masses referred to commercially as amorphous graphite.

Graphite was at one time confused with other minerals of similar appearance, chiefly molybdenite, MoS_2. One common name for graphite is plumbago (leadlike). Until modern times users thought that it contained lead. In 1565 graphite was reported as a separate mineral and referred to as Stimmi Anglicum (1). Carl Scheele demonstrated in 1779 that graphite oxidized to CO_2, thus proving it to be a form of carbon. In 1789 Abraham Werner named it graphite from the Greek *graphein*, to write. The now depleted Borrowdale graphite mines in Cumberland, UK, opened ca 1564 and produced graphite for pencils, called capucines.

One useful classification of graphite depends on the mode of formation that leads to three physically distinct common varieties: flake, lump, and amorphous. The term flake is self-explanatory; flake forms occur disseminated in rock. Lump graphite occurs in fissure-filled veins in pegmatite dikes, also associated with chip and the rarer needle forms. Amorphous graphite occurs in beds that were once coal, but fine-grained, easily ground vein graphite is also classified as amorphous.

All graphite has crystal structure but only certain kinds and sizes of natural graphites are commercially classified as crystalline, a term used for import duty purposes. Throughout this article reference is made separately to flake, vein (lump or high crystalline), and amorphous forms, all of which are essentially the same crystalline form of carbon. However, fine structured graphites (cryptocrystalline (2)) have been classified as amorphous.

Structure

Parallel layers of condensed planar C_6-rings constitute the graphite crystallite. Each carbon atom joins to three neighboring carbon atoms at 120° angles in the plane of the layer. The C–C distance is 0.1414 nm (this bond is 0.1397 nm in benzene); the width of each C_6-ring is 0.2456 nm. Weak van der Waals forces pin the carbons in adjoining layers, thus accounting in part for the marked anisotropic properties of the graphite crystal. Figure 1 shows a Laue x-ray diffraction pattern of a single natural graphite crystal.

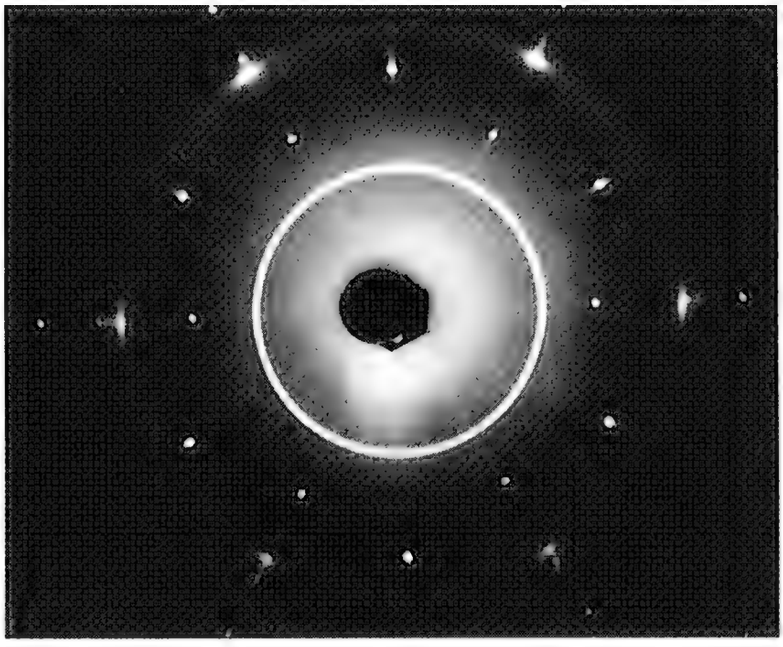

Fig. 1. Laue x-ray diffraction pattern of a single natural graphite crystal.

In the completely graphitized crystallite the planar C -layers stack in ordered parallel spacing 0.33538 nm apart at room temperature. The hexagonal form of graphite (Fig. 2) contains the most common stacking order: ABABAB. ... A small percentage of graphites exhibit ABCABCABC ... stacking order (Fig. 3), resulting in the rhombohedral form. Grinding increases the rhombohedral structure, probably through pressure. Heating above 2000°C transforms the rhombohedral structure to hexagonal, suggesting that the latter is more stable. Impact from explosion can convert rhombohedral graphite- to cubic-structured carbon, ie, diamond (see CARBON, DIAMOND, SYNTHETIC).

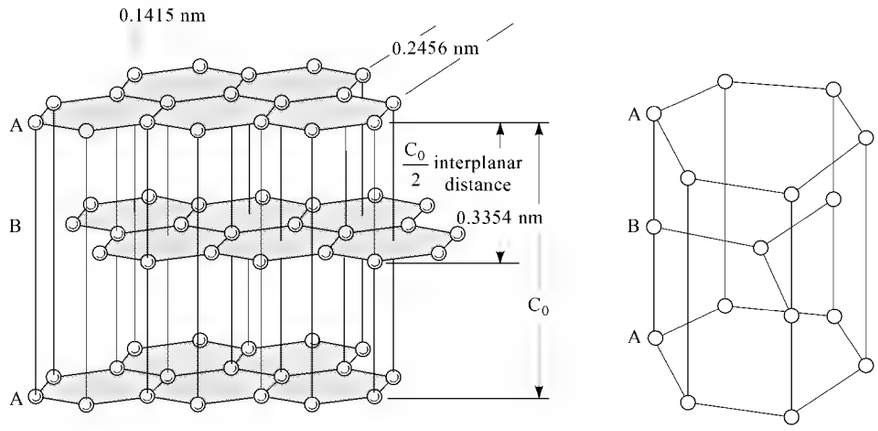

Fig. 2. Hexagonal structure of graphite.

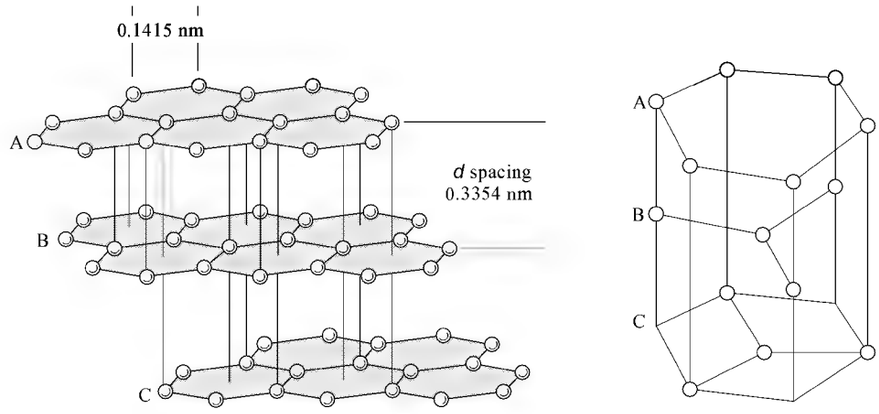

Fig. 3. Rhombohedral structure of graphite.

Grinding graphite to particle sizes smaller than ca 0.1 μm reduces the crystallite size to less than 20 nm, at which size two-dimensional ordering replaces the three-dimensional ordering of graphite. The weakened pinning forces permit the planar layers to move further apart and assume progressively random, though parallel, positions with respect to each other. This turbostratic structure is the characteristic structure of the so-called amorphous carbon that is found in chars. At more than 0.344 nm *d* spacing, the parallel planar C -layers assume a completely random lateral ordering. When playing cards are bunched into a deck, without evening the sides and ends for redealing, the deck represents turbostratic structure, the structure of amorphous carbon. The parallel cards have no order in the third dimension of the deck. Turbostratic structure requires that each layer (card) in the bunched, uneven deck be separated further than in the evened deck of hexagonal structure, and at a minimum of 0.344 nm. Table 1 depicts the effect of different *d* spacings on graphite structures.

Table 1. Effect of Progressive Grinding of Graphite

Sample	Specific surface area, m^2 g	Crystallite Thickness, L_c, nm	Crystallite Diameter, L_a, nm	*d* Spacing, nm
3-μm Sri Lanka (Ceylon) graphite (Dixon 200-10)	11.5	>100	>100	0.3354
Sri Lanka graphite	409	17.2	41.6	0.3356
Sri Lanka graphite	580	0.9		0.378
Sri Lanka graphite	699	0.9		0.380
Monarch 71 carbon black	350	1.5	2.5	0.400

The physical properties of finely ground but highly oriented natural graphites, such as 5-μm Sri Lanka (Ceylon) graphite, differ from those of turbostratic carbons such as chars, carbon blacks, or carbons formed from heavily ground graphites. Figure 4 is an electron micrograph of 5-μm Sri Lanka graphite; the straight edges and angles of the particles contrast sharply to the rounded shapes of carbon black particles (see CARBON, CARBON BLACK).

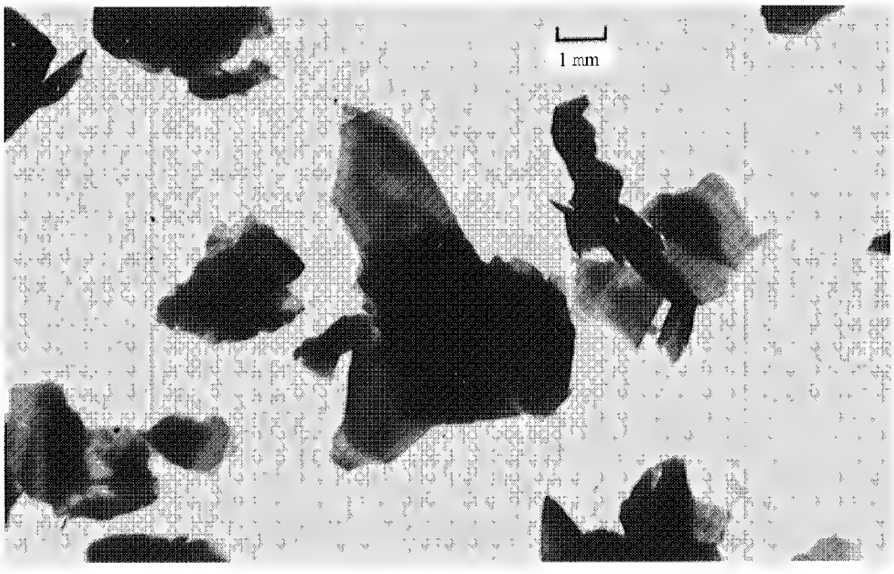

Fig. 4. Electron micrograph of Sri Lanka (Ceylon) graphite.

Physical Properties

Solid articles made of natural graphite always require a binder; ie, they are always composites. The influence of the binder, the processing, and the kind of graphite used, together with graphite's strong anisotropism, influence the properties of the composites. In general, the overall quantities are usually greater than those measured along the *a* axis or along the *c* axis of the graphite under consideration. Table 2 lists some of the physical properties of natural graphite.

Table 2. Physical Properties of Natural Graphite[a]

density[b], g/mL	
calculated	2.265
experimental, pure Sri Lanka	ca 2.25
compressibility, N/m^2[c], Sri Lanka	
at low pressures	4.5×10^{-11}
at high pressures	$<2 \times 10^{-11}$
average	3.1×10^{-11}
shear modulus, N/m^2[c]	2.3×10^{9}
Young's modulus, N/m^2[c]	1.13×10^{14}
heat of vaporization[d], kJ/mol[d]	711
sublimation point, K	4000–4015
triple point, K	
graphite–liquid–gas, 101.3 kPa[e]	3900 ± 50
graphite–diamond–liquid, 12–13 GPa[e]	4100–4200
surface energy, J/cm^2[d]	ca 1.2×10^{-5}

[a] Ref. 3.

[b] The difference between the calculated and experimental values of density is caused by dislocations and imperfections.

[c] To convert N/m^2 to dyn/cm^2, multiply by 10.

[d] To convert J to cal, divide by 4.184.

[e] To convert kPa to atm, divide by 101.3.

Graphite's strength increases as the temperature rises. Relief of frozen-in stresses up to ca 2500°C accounts for this unusual property. Plastic deformation occurs above 2500°C. The coefficient of linear expansion along the *a* axis changes from slightly negative below 383°C to slightly positive above that temperature; its average along the *c* axis is 238×10^{-7} between 15 and 800°C.

The thermal conductivity, W/(m·K), along the *a* axis reaches a maximum of 285 at −100°C and falls rapidly with declining temperature. It is 251 at 20°C. Along the *c* axis it remains ca 837 to very low temperatures. The specific heat varies markedly with temperature (Fig. 5). The steep rise in C_p above 3500 K probably results from reversible formation of vacancies or other thermal defects (4).

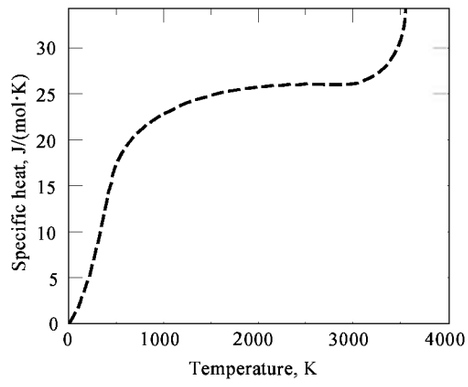

Fig. 5. Specific heat of solid graphite.

In thin sections natural graphite is translucent, strongly pleochroic, and uniaxial. It has a negative sign of birefringence and two extinctions per revolution under crossed Nicol prisms. The atomic number of carbon accounts for its low absorption coefficient for x-rays and electrons.

Single graphite crystals exhibit strong temperature-dependent anisotropic properties, both electrical and magnetic. However, this is of academic interest because natural graphite products are not single crystals. Flake graphites enhance anisotropy in bodies where forming processes such as extrusion, pressing, or jiggering align the flakes.

The specific resistance of natural graphite crystals is ca 10^{-4} Ω·cm (room temperature) along the *a* axis parallel to the network basal plane. The resistance along the *c* axis (perpendicular to the basal plane) is ca 1 Ω. The *c*/*a* axis anisotropy ratio is, therefore, ca 10^4. Screw dislocations within the crystal may short-circuit the current path parallel to the *c* axis and cause lower anisotropic ratios; separation of planes may cause higher anisotropic ratios.

Graphite is strongly diamagnetic because of its abundance of π electrons. Grinding the crystallite smaller than 20 nm creates a deficiency in π electrons and thus destroys the diamagnetism. The value of the specific magnetic susceptibility for Sri Lanka graphite is ca -6.5×10^{-6} at 20°C, -0.5×10^{-6} along the *c* axis and -22×10^{-6} along the *a* axis where it is temperature independent.

Chemical Properties

Graphite burns slowly in air above 450°C, the rate increasing with temperature and exposed area. The particle size and shape govern the ignition temperature. Flake graphites generally resist oxidation better than granular graphites.

Above 800°C graphite reacts with water vapor, carbon monoxide, and carbon dioxide. Chlorine has a negligible effect on graphite, and nitrogen none. Many metals and metal oxides form carbides above 1500°C. These reactions occur with the carbon atom and destroy the graphitic structure (see CARBIDES). A series of compounds in which the graphite structure is retained, known as graphite compounds, consist of two general kinds: crystal and covalent compounds.

Graphite can be regenerated from the crystal compounds because the graphitic structure has not been too greatly altered. The dark crystal compounds are called intercalation compounds, interstitial compounds, or lamellar compounds because they are formed by reactants that fit in between the planar carbon networks. Each interlayer may be occupied, or every other interlayer, or every third interlayer, etc. Thus the same element, or group, can form a series of distinct compounds. The alkali metals form a variety of such addition compounds: potassium, rubidium, and cesium reactions with graphite are well known. The compounds of sodium and lithium are less well known. When potassium vapor enters graphite interstitially, it forms a series of intercalation compounds such as C_8K *[12081-88-8]*, $C_{24}K$ *[12100-36-6]*, C_3K *[12103-59-2]*, and others depending on the sequence of interstitial layers filled.

The C_8K and $C_{24}K$ compounds have an unusual ability to absorb hydrogen, nitrogen, and methane. C_8K catalyzes room-temperature additions of primary and secondary amines to dienes, yielding alkenyl amines. These compounds form by stepwise additions of potassium at increasing vapor pressures. Often several identical treatments are required to complete the reaction stoichiometrically, depending on the particle size of the graphite used. The colors become progressively lighter as the amount of metal constituent increases, from black through blue to bronze.

Compounds of graphite with alkali metals or ammonia are electron donors: the electrical resistance decreases, from that of the original graphite, and the Hall coefficient remains negative. Compounds with the halogens (except fluorine), metal halides, and sulfuric acid (graphite sulfate) are electron acceptors. The electrical resistance decreases but the Hall coefficient changes from negative to positive (5).

Graphite sulfate, long known and early investigated, forms when graphite is warmed in concentrated sulfuric acid containing a small quantity of an oxidizing agent such as concentrated nitric acid. The graphite swells and becomes blue. The compound, approximately $C^{+}_{24}(HSO_4)\ ;\ \cdot 2H_2SO_4$ *[12689-13-3]*, hydrolyzes at once in water and the graphite is recovered. The recovered, washed, and dried graphite exfoliates when quickly heated, in the manner of Pharaoh's Serpents (mercuric thiocyanate). Graphite sulfate also forms at the graphite anode while electrolyzing strong sulfuric acid. Turbostratic carbons do not react this way.

Bromine vapor forms C_8Br *[12079-58-2]* by direct addition to well-oriented graphite. Other halogen and mixed halogen compounds have been prepared.

Some intercalated crystalline compounds find their way into commerce as catalysts for chemical synthesis. Graphite–$FeCl_3$–KCl *[56591-80-1]* has been used in the synthesis of ammonia (qv). A series of patents were assigned to the Sagami Chemical Research Center (Japan) dealing with graphite complex catalysts for chemical synthesis (6). Acetic acid (qv) has been synthesized in high yield from methanol and carbon monoxide over a graphite–$RhCl_3$–I_2 compound.

The covalent compounds of graphite differ markedly from the crystal compounds. They are white or lightly colored electrical insulators, have ill-defined formulas and occur in but one form, unlike the series typical of the crystal compounds. In the covalent compounds, the carbon network is deformed and the carbon atoms rearrange tetrahedrally as in diamond. Often they are formed with explosive violence.

Graphite oxide *[1399-57-1]*, graphitic acid, was prepared and described by Sir Benjamin Brodie in 1859. He heated graphite with a mixture of potassium chlorate and concentrated nitric acid (Brodie's reagent) on a water bath for four days and then repeated the treatment several times after-intervening washings and dryings. The process yielded a stable yellow substance that retained the general physical form of the original graphite. It consisted of carbon, hydrogen, and oxygen and it reddened litmus. Since the Brodie method is extremely dangerous, graphite oxide is more safely prepared in the cold by Staudenmaier's method: digesting graphite with a mixture of nitric acid, sulfuric acid, and potassium chlorate. The compound also forms on a graphite anode during electrolysis of a dilute sulfuric acid solution containing an oxidizing compound such as nitric acid. The structure is unknown.

Graphite oxide may explode when heated above 200°C. Below this temperature it converts to a black powder once known as pyrographitic acid. The composition varies with the heat treatment and the end point; according to x-ray diffraction studies it is a form of carbon that reconverts to well-ordered graphite on heating to 1800°C. Before the use of x-rays, chemists used the Brodie reaction to differentiate between graphitic carbons and turbostratic carbons. Turbostratic carbons yield a brown solution of humic acids, whereas further oxidation of graphite oxide produces mellitic acid (benzenehexacarboxylic acid) *[517-60-2]*, $C_{12}HO_{12}$.

Fluorine forms covalent compounds with graphite. C_4F *[12774-81-1]* is prepared by exposing graphite to a mixture of fluorine and hydrogen fluoride at room temperature. Heating graphite fluoride at ca 400°C forms CF *[12069-59-9]*, a gray solid wetted neither by water, alcohol, benzene, nor acetone. These fluorine compounds of graphite explode on heating.

Graphite fluoride continues to be of interest as a high temperature lubricant (6). Careful temperature control at 627 ± 3°C results in the synthesis of poly(carbon monofluoride) *[25136-85-0]* (6). The compound remains stable in air to ca 600°C and is a superior lubricant under extreme conditions of high temperatures, heavy loads, and oxidizing conditions (see LUBRICATION AND LUBRICANTS). It can be used as an anode for high energy batteries (qv).

The fullerenes are related to graphite even though they are not graphite compounds, but rather are a separate class of carbonaceous materials. Fullerenes have complex configurations of approximately 60 or more carbon atoms, the best known of which are shaped like a soccer ball (C_{60}). A preparation method for fullerenes involving heating graphite rods in a vacuum chamber and collecting the fullerene-rich soot deposited on the chamber surfaces was a significant breakthrough because of the large yields of the materials (7).

Geographic Occurrence

Table 3 summarizes the world's production of natural graphite for 1986–1988 (9). As of 1990, the deposits of significant commercial interest were limited to those of Sri Lanka (Ceylon), Madagascar, Mexico, Canada, Brazil, Germany, Austria, the Republic of Korea, Norway, Russia, Ukraine, People's Republic of China, and Zimbabwe.

Table 3. World Production by Countries[a], t

Country	1986	1987	1988[b]
Argentina	40	216	24
Austria	36,167	39,391	7,577
Brazil (marketable)[c]	28,586	31,404	32,000
Burma[d]	722		
Canada	200	1,900	4,700
China[e]	185,000	185,000	200,000
Czechoslovakia[e]	25,254[f]	25,000[g]	25,000[g]
Germany	13,233	9,891	7,000[e]
India (mine)[h]	38,412	42,589	52,134
Korea, North[e]	25,000	25,000	25,000
Korea, Republic of			
amorphous	96,577	106,507	107,767
crystalline flake	641	838	678
Madagasdar	16,187	13,169	14,106
Mexico			
amorphous	36,018[g]	36,674	42,096
crystalline flake	1,838	1,787	1,735
Norway[i]			
Romania[e]	12,000	12,000	12,000
Russia[e,j]	83,000	84,000	84,000
Sri Lanka	7,453	9,400	8,547
Turkey (mine)	3,586	11,760	12,833
Zimbabwe	15,004	13,530	11,441
Total	*624,918*[g]	*650,056*[g]	*648,638*

[a] Table includes data available through May 8, 1990 (8).

[b] Preliminary.

[c] Does not include the following quantities sold directly without beneficiation, in metric tons: 1985–16,425; 1986–19,074; 1987–10,505; 1988–20,000 (est); and 1989–20,000 (est).

[d] Data are for fiscal year beginning Apr. 1 of that stated.

[e] Estimated.

[f] Reported figure.

[g] Revision.

[h] Indian marketable production is 10–20% of mine production.

[i] Production resumed after 1988.

[j] Includes production from the Ukraine and other republics of the former Soviet Union.

The three physically different forms of natural graphite, which provide essentially different commodities, are in Sri Lanka (lump), Madagascar (flake), China (flake and amorphous), Brazil (flake), Zimbabwe (flake), Germany (flake), Norway (flake), Mexico (amorphous and flake), and the Republic of Korea (amorphous).

Sources in Asia.

China. China is the world's largest graphite source and usually the price-setter. The great majority of Chinese graphite is produced in Shandong and Heilongjiang Provinces, and much smaller amounts are produced in Inner Mongolia and Shanxi Provinces. Most of the production is crystalline flake and most of the mines are open-pit. The two largest mines are the Nan Shu and the Bai Shu, both in Shandong Province, and a third significant mine is the Liu Mao in Heilongjiang Province.

India. Most Indian production occurs in the States of Orissa and Rajasthan and is used domestically.

Korea. More graphite is mined on the Korean peninsula than any other region in the world, except China. Geologists estimate the reserves of both flake and amorphous, but predominantly amorphous, graphite on the order of millions of tons. The iron content of Korean graphite is low and the ash is a distinctive white.

Sri Lanka. Sri Lanka, formerly Ceylon, contains the largest known deposits of lump (vein) graphite. It occurs in a large area in the southwestern part of the island in metamorphosed Archean sediments known as the Khondalite system. In 1971 the Sri Lankan government nationalized the three operating mines as The State Graphite Corporation. Sri Lankan graphite is usually completely graphitized and contains both quartz and sulfides. It is favored for lubricants, pencils, and electromotive brushes.

Sources in Europe.

Austria. Two distinct mineralogical regions, Styria and lower Austria, combine to make Austria one of Europe's larger producers of natural graphite. As in all other European deposits, the graphite originated through metamorphosis of carboniferous and bituminous substances. Therefore, the deposits occur in small, lean lenses. With one exception it is mined underground.

Germany. The Passau district of Bavaria has long produced crystalline flake graphite suitable for crucibles such as those used by alchemists in the Middle Ages. In 1250 the inhabitants of Pfaffenreuth were required to pay their tithe with graphite. Today, Graphitwerk Kropfmuehl A.G. produces flake graphite of high purity suitable for crucibles, pencil leads, and lubricants. The country rock is part of the "kristallines Grundgebirge," the old gneissic and schistose rocks of the Bohemian basin. The ore contains 20–25% graphite and is beneficiated and processed by flotation, grinding, and sieving.

Norway. A S Skaland Grafitverk, on Senja Island, is the only operating crystalline flake mine in Norway.

Spain. Although Spain produces little or no graphite, large deposits occur in the province of Jaen and near Toledo.

Sources in Africa.

Madagascar. The island of Madagascar is an important source of crystalline flake graphite of large size and high quality. The widespread reserves are believed to be exceptionally large. The deposits are found with lateritic deposits of iron and bauxite. Graphite, which is resistant to weathering, is found in the weathered residue; thus the graphitic content of 3–10% has been increased by natural leaching. The flake is large, strong, and flexible and is the best graphite for many refractories. The pyrometric cone equivalent (PCE) of the ash runs from cone 16 to cone 20, higher than the PCE of other flake graphite ashes, indicating that it is more refractory.

Zimbabwe. This country has one large crystalline flake graphite mine, the Lynx, located between Harare and Lake Kariba. The mine is underground and is being mined on four levels for ore averaging 35% carbon.

Sources in North America.

Canada. Canada has one sizeable mine and at least five more possibly commercial deposits, one or two of which might be brought onstream in the next few years. The new Lac-des-Iles mine and mill of Stratmin Inc. has, for practical purposes, displaced Asbury Graphite's older and smaller mine and mill at Notre Dame du Laus. Stratmin states that the capacity of the operation is 25,000 tons per year as concentrate and this might be substantially increased later.

Mexico. The state of Sonora contains extensive deposits of quality amorphous graphite. There exists, *lit-par-lit*, as many as seven distinct beds of graphite with alternating layers of metamorphosed andalusite-bearing Triassic rocks. The mines lie about 400 km south of the U.S. border in the region of Moradillas, and several prospects lie further east and south. The mineral suite includes micas, clay minerals, tourmaline, and hematite. Pyrite and gypsum are sometimes found. There are considerable dissimilarities in the products of different mines in the mineral suite and the degree of graphitization. In addition, there is a sizeable crystalline flake graphite mine near Telixtlahuaca, Oaxaca State. Several more deposits of crystalline flake exist in Oaxaca, one of which may be developed.

Sources in South America.

Brazil. Brazil has two principal crystalline flake mines, a smaller one at Itapecerica and a larger one at Pedra Azul, both in Minas Gerais State. Both mines are owned by Nacional de Grafite Ltd. The ore at Itapecerica averages 20% carbon and is surface mined from a number of pockets spread over an area of ca 129.5 km^2 (50 square miles). The ore at Pedra Azul averages 7% carbon, is larger flaked than the other, and is disseminated in heavily weathered gneissic rock.

Identification of Graphite Ores

The ability to identify the source of the graphite depends on what is present in the ore. In practice, samples are nearly always milled to a powder. It is possible, up to a point, for an experienced technologist to distinguish graphite from various commercial sources merely by inspection. As the samples submitted for examination become more and more finely divided in the course of manufacturing and milling operations, the difficulty in making these decisions becomes progressively greater.

Finely divided samples may be identified further by analyses of the graphite ash, and identification of the minerals associated with the graphite and comparison with graphites from known sources. Owing to its softness and opaqueness, most of the graphitic carbon must be removed from the sample before analysis by either method. There are two general ways of accomplishing this.

In the first, the sample of graphite is ignited gently at 800°C until all the graphitic carbon is consumed, leaving the calcined gangue material. This includes the interlaminated material as well as the larger fragments, some of which may be country rock or lithic fragments as contrasted with minerals indigenous to the graphite deposit. This ash may be separated into light and heavy fractions with a heavy liquid, such as bromoform, or the fines, which constitute the bulk of the ash, may be decanted by repeated flushings with water. The residual material or the minerals separated with a heavy liquid can then be examined under a binocular, petrographic microscope for comparison with known ores.

The disadvantage of this procedure is that the minerals may be physically or chemically altered during burning. For example, the refractive index of clay minerals is changed; the color, birefringence, and pleochroism of micas is altered; carbonates are destroyed; and the iron sulfides are oxidized to iron oxides.

To avoid these alterations in the mineral suite, untreated graphite is separated from the accompanying minerals by immersing the sample in a liquid of density intermediate to that of the bulk of the graphitic carbon and the gangue minerals, which then sink together with certain composite grains of graphite attached to a heavy mineral. The specific gravity at which this separation is best effected varies with different graphite samples, but 2.40 is usually satisfactory. About 10 g of graphite is strewn over the surface of about 50 mL of the heavy liquid in a Spaeth sedimentation glass. The slurry is stirred and covered and the whole allowed to stand quietly away from sudden temperature changes until a separation takes place, which may require >1 2 h. After separation, the stopcock is turned to the position that retains the heavy mineral concentrate, the light fraction is completely removed from the glass, and the bulk of the heavy liquid is recovered. The concentrate is transferred to a small beaker, washed with benzene, and dried. It is then ready for inspection with the microscope. Often the separated heavy mineral residue grains will be coated with a film of graphite that may interfere with their identification. In such cases the crop may be cautiously washed with soap and water to remove most of the graphite film and then dried. The interlaminated impurities of the graphite flakes, needles, and folia are not included in the sink portion. Since this fraction is usually too finely grained for useful observation, its loss is not serious.

The methods outlined are, in general, preferred among the methods in use for identifying commercial milled graphites by color of ash, grit, color of mark, and feel.

Chemical Analysis

There are no generally accepted methods for the complete analysis of natural graphite. Industrial methods usually emphasize either the carbon content or analysis of the ash. Although the carbon percentage is of considerable importance, it is usually true that the mineral suite is more significant for a specific use, eg, fluxing constituents in graphite must be avoided for refractory uses, and abrasive minerals in graphite must be absent for lubricating uses. Associated minerals are seldom reported other than as "ash."

The simplest analytical procedure is to oxidize a sample in air below the fusion point of the ash. The loss on ignition is reported as graphitic carbon. Refinements are determinations of the presence of amorphous carbon by gravity separation with ethylene bromide, or preferably by x-ray diffraction, and carbonates by loss of weight on treating with nitric acid. Corrections for amorphous carbon and carbonates are applied to the ignition data, but loss of volatile materials and oxidation may introduce errors.

Graphite is frequently, although incorrectly, analyzed by the proximate method used for coal in which the volatile material is determined by strongly heating the sample in a covered or luted crucible. Some oxidation of the graphite always occurs so that the value obtained for volatile matter is high and thus the "fixed carbon" is too low. The method lacks both accuracy and precision.

The best indirect, but seldom used, method is to determine the total moisture separately in a Penfield tube, determine the loss on ignition in air at 825–875°C, and report graphitic carbon as percent loss on ignition (100 %moisture %ash). It is desirable to use a platinum dish for ignition loss and it

is necessary to spread the graphite in a thin layer. Thermogravimetric analysis (tga) is also used to determine weight losses of free moisture and other volatiles as well as graphite oxidation.

All too often specifications reflect a lack of understanding of what is required of the graphite purchased. Volatile matter, for instance, may be a factor where the graphite is to be heated in use but volatiles are of no significance for mechanical uses at room temperature. Percent "ash" may be far less important than the material responsible for the ash. An artificial graphite, for instance, whose total ash is 0.5% silicon carbide, may be an inferior lubricant to a natural graphite whose total ash is 5.0% fine mica and clay. The results of chemical analysis of graphite residues given in Table 4 were obtained by closely following the conventional methods for silicate rocks (see SILICA).

Table 4. Analysis of Graphite Residues From Principal Sources

Component	Percent of component in			
	Sri Lanka, "90%"[a]	Madagascar, "86%"	Korean, "83%"	Mexican, "82%"
SiO_2	57.50	46.26	52.05	50.85
Al_2O_3	6.54	33.16	32.11	29.42
Fe_2O_3	25.07	16.73	4.92	11.74
MgO	1.09	1.46	1.96	0.48
CaO (SrO)	4.63	0.22	1.64	0.73
Na_2O	0.41	0.08	0.68	0.60
K_2O	0.68	0.95	5.05	4.78
CO_2	present			
TiO_2	0.41	0.80	1.58	1.27
P_2O_5	0.09	0.17	0.06	0.06
SO_3	0.41	trace		trace
F	0.05			
S (FeS_2)	4.22			
MnO	0.16	0.38	0.04	0.05
BaO	0.06		0.10	0.06

[a] "90%" graphite also contains 0.13% Cu; trace of Pb; 0.014% Zn; 0.016% Ni; 0.011% Co; trace of Zr; trace of As; 0.07% Cr; no Se; no Te.

A method for physically separating turbostratic carbon and graphite involves shaking a sample into suspension in ethylene bromide of sp gr 2.17 and centrifuging. The method is unreliable except where fine carbon and coarse graphite are admixed; it can be an aid in qualitative examination.

The percentage of turbostratic carbon in a graphite sample can be estimated after determining the average *d* spacing of x-ray diffraction (10).

Eight ASTM methods exist for testing graphite, plus a number more that apply to carbon and graphite (Table 5).

Table 5. ASTM Graphite-Related Test Methods, Specifications, Recommended Practices, and Definitions[a]

Designated number	Title
C560	Methods for Chemical Analysis of Graphite
C561	Test Method for Ash in a Graphite Sample
C562	Test Method for Moisture in a Graphite Sample
C611	Test Method for Electrical Resistivity of Manufactured Carbon and Graphite Articles at Room Temperature
C695	Test Method for Compressive Strength of Carbon and Graphite
C714	Test Method for Thermal Diffusivity of Carbon and Graphite by a Thermal Pulse Method
C747	Test Method for Moduli of Elasticity and Fundamental Frequencies of Carbon and Graphite Materials by Sonic Resonance
C748	Test Method for Rockwell Hardness of Fine-Grained Graphite Materials
C749	Test Method for Tensile Stress–Strain of Carbon and Graphite
C816	Test Method for Sulfur in Graphite by Combustion–Iodometric Titration Method
C886	Method for Soleroscope Hardness Testing of Fine-Grained Carbon and Graphite Materials
D561	Test for Ash in Graphites
D1367	Lubricating Qualities of Graphites
D1553	Analysis of Graphites Used as Lubricants

[a] Includes only items with the word "Graphite" in the title.

Specifications

The ASTM publishes specifications, recommended practices, and definitions for graphite, as has the U.S. Government (11,12). Domestically used flake is classified according to purity with high grade containing 95–96% carbon, and low grade 90–94% carbon. High purity crystalline flake contains 99% carbon and above. Sri Lanka graphite is classified according to lump, chip, and dust with subclassifications. Amorphous graphite is classified according to locality and carbon content, seldom higher than 85%. The variety of specifications exists because graphite is found worldwide, is mined by many small establishments, and is subject to keen competition among suppliers. Table 6 lists the principal U.S. suppliers of natural graphite.

Table 6. U.S. Suppliers of Natural Graphite

Company	Location	Grade
Asbury Graphite Co.	Asbury, N.J.	all grades
Cummings-Moore Graphite Co.	Detroit, Mich.	amorphous
Dixon Ticonderoga Co.	Lakehurst, N.J.	all grades
Southwestern Graphite Div.	Burnet, Tex.	flake
Superior Graphite Co.	Chicago, Ill.	all grades

Economic Aspects

For some uses natural graphite is a strategic commodity since no substitutes exist. Imports account for all of the strategic natural graphite used in the United States. Published prices cover a wide range of specifications (Table 7). Individual companies vary selling prices by kinds, sizes, and mixtures, depending on the method and extent of physical conditioning. Since the graphite business is highly competitive, both supplier and consumer show a reluctance to discuss negotiated prices. U.S. import duties on natural graphite are shown in Table 8.

Table 7. Graphite Prices[a]

	1988, $/t	1989, $/t
Industrial Minerals		
crystalline large flake, 85%–90% carbon	820–1300	820–1300
crystalline medium flake, 85%–90% carbon	770–1120	770–1120
crystalline small flake, 80%–90% carbon	540–900	540–900
powder, 74 μm[b], 95%–97% carbon	770–1000	770–1000
powder, 74 μm[b], 97%–99% carbon	1000–1300	1000–1300
amorphous powder, 80%–85% carbon	220–440	220–440
custom value, at foreign ports		
flake	742	951
lump and chip, Sri Lankan	843	1027
amorphous, Mexican	53	114

[a] Refs. 13 and 14.

[b] 74 μm = 200 mesh.

Table 8. U.S. Import Duties[a]

Tariff item	Number	Most favored nation (MFN)	Non-MFN
crystalline flake, (not including flake dust)	2504.10.10	0.7 ¢/kg	3.6 ¢/kg
other powder	2504.10.50	free	10% ad valorem
other	2504.90.00	free	10% ad valorem

[a] Jan. 1, 1990.

Uses

The many useful properties of graphite give rise to a wide variety of products: unctuous, dry lubricant; marks readily, writing and drafting pencils; combination of lubricity and electrical conductivity, motor and generator brushes; excellent weathering properties and inertness, industrial paint pigment; solubility in molten iron, carbonraiser for steel; poorly wet by most metals and alloys, foundry mold facings; and burns slowly, conducts heat, and retains strength over a large temperature range, refractories such as crucibles, carbon–magnesite brick, continuously casting ware, and stopper heads for steel ladles. Some additional properties of interest include hydrophobicity, forms water-in-oil emulsions, carries a negative charge, has low photoelectric sensitivity, is strongly diamagnetic, and is an infrared absorber.

Table 9 lists the quantities and dollar values of natural graphite used in the United States in 1988–1989 by product groups (7,15). Refractories and crucibles account for about half of the known use. Natural graphite has its next greatest use (ca 15%) in lubricants and packings, including expandable graphite.

Table 9. U.S. Consumption of Natural Graphite, By Use

	Crystalline		Amorphous[a]		Total[b]	
Use	Quantity, t	Value, 10^3 $	Quantity, t	Value, 10^3 $	Quantity, t	Value, 10^3 $
1987[c]						
	13,132	14,795	16,046	9,082	29,178	23,876
1988						
batteries	d	d	d	d	804	1,340
brake linings	2,601	1,948	2,494	3,107	5,095	5,055
carbon products[e]	317	879	232	374	549	1,253
crucibles, retorts, stoppers, sleeves, nozzles	d	d	d	d	1,641	1,818
foundries[f]	465	283	3,907	1,247	4,373	1,530
lubricants[g]	3,386	4,895	2,815	1,623	6,201	6,518
pencils	1,596	1,947	303	174	1,899	2,121
powdered metals	1,450	1,472	50	84	1,500	1,556
refractories	d	d	d	d	7,382	4,352
rubber	95	128	338	324	434	452
steelmaking	188	116	1,153	1,405	1,341	1,521
other[h]	2,533	5,655	455	677	2,988	6,332
withheld uses	7,267	6,848	2,560	663		
Total[b]	*19,897*	*24,171*	*14,308*	*9,678*	*34,205*	*33,848*
1989						
batteries	d	d	d	d	1,243	1,924
brake linings	2,281	2,436	2,427	5,450	4,708	7,886
carbon products[e]	340	886	167	242	507	1,128

crucibles, retorts, stoppers, sleeves, nozzles	d	d	d	d	1,497	1,697
foundries[f]	408	481	4,847	1,412	5,255	1,893
lubricants[g]	3,391	5,033	3,125	1,068	6,516	6,101
pencils	1,757	1,876	248	150	2,005	2,026
powdered metals	1,401	2,551	58	111	1,459	2,662
refractories	d	d	d	d	10,195	8,985
rubber	72	108	406	314	478	422
steelmaking	218	122	1,035	484	1,253	606
other[h]	2,108	7,542	189	284	2,297	7,826
withheld uses	7,917	9,552	4,005	2,160		
Total[b]	*19,893*	*30,587*	*16,507*	*11,675*	*37,413*	*43,156*

[a] Includes mixtures of natural and manufactured graphite.

[b] Data may not add to totals shown because of independent rounding.

[c] Revision reflects a data correction in the lubricant and other use categories.

[d] Withheld to avoid disclosing company proprietary data; included with "Withheld uses."

[e] Includes bearings and carbon brushes.

[f] Includes foundry facings.

[g] Includes ammunition, packings, and seed coating.

[h] Includes paints and polishes, antiknock and other compounds, soldering and/or welding, electrical and electronic products, mechanical products, magnetic tape, small packages, industrial diamonds, and drilling mud.

Refractories. Natural graphite refractories are either formed and fired ware such as crucibles, shapes such as carbon–magnesite brick and continuous casting ware, or ramming mixes. Graphite imparts high refractoriness, low thermal expansion, excellent heat-shock resistance, high resistance to metal and flux attack, resistance to wetting by molten substances, increased strength and resilience at elevated temperatures, and high thermal and electrical conductivity. The purity of refractory graphite is ca 80–90% graphitic carbon (see REFRACTORIES).

Most ramming mixes contain amorphous graphite. The refractory ware group consists chiefly of crucibles for melting metals and alloys, carbon–magnesite brick for lining furnaces, converters and ladles, alumina–graphite continuous casting ware for holding and moving hot metal, stoppers and nozzles for steel pouring ladles, and a miscellaneous group of saggers, slabs, rods, stirrers, and skimmers. Crystalline flake graphite is used almost exclusively because it burns slower than other graphites, suffers less from attrition in manufacturing processes, and imparts a desirable physical structure through orientation of the flake in the forming processes.

The disadvantage of graphite is that it burns slowly in an oxidizing atmosphere so that some refractories require glazes. Manufacturers bond their ware with either refractory clays or mixtures of tars and pitches to form a coke bond. Crucibles for nonferrous use contain a percentage of silicon carbide; carbon-bonded crucibles run higher in silicon carbide and use finer flake graphite. Graphite for ferrous use contains no silicon carbide because iron attacks it at pouring temperatures (see CARBIDES).

Crucibles usually contain 30–50% flake graphite. Stoppers and nozzles, used in bottom-pour ladles to control the flow of molten steel into molds, contain ca 20–30% flake graphite; nozzles may contain as much as 40%. The advantage of graphite stoppers and nozzles to nongraphitic products is their superior heatshock resistance, their resistance to the erosion of flowing steel, and their property of withstanding deformation without rupture at operating temperatures.

Foundry facings consume a large tonnage of natural graphite, primarily amorphous. Foundry facings are carbonaceous or mineral powders applied to the surface of sand molds to prevent the molten metal from penetrating into or reacting with the sand. Generally, clay binders are applied dry to green sand molds whereas organic binders are applied wet to dry sand molds.

The use of carbon–magnesite brick increased greatly in the 1980s, mostly at the expense of magnesia and magnesia–chrome refractories. The bricks are mainly used to line basic oxygen converters, in the slag-lines and water-cooled side-walls of electric arc furnaces, and more recently, to line steel ladles. The graphite content of carbon–magnesite bricks can range from 8% to 30%, depending on the type of brick. The bricks have come into such great use because of the higher temperature, and the longer dwelling time at these temperatures, now common in steelmaking, and particularly because of a need for greater thermal-shock resistance. These refractories also have longer use lives than those they replaced.

Alumina–graphite refractories, almost all continuous casting ware, have come into much greater use as continuous casting has spread in steelmaking. These refractories are used in shrouds that conduct the molten metal from the ladle to the tundish, in the subentry tubes that take the metal from the tundish to the mold, in isostatically pressed stopper rods, and in shroud tubes for slab and bloom casters. The alumina–graphite compositions are used in these products because of the thermal-shock resistance and corrosion resistance they impart to the product.

Lubrication. The slip that readily occurs between layers of graphite planes only partially explains graphite's dry lubricating properties. A suitably adsorbed film such as water must also be present; without it graphite ceases to lubricate and may, though rarely does, become abrasive (16). Scrolls (rolled-up layers 1–5 nm) may play a part in the lubricity of graphite by acting as rollers between the planar layers.

Graphite lubricants include the dry powder, admixtures with liquid lubricants or greases, volatile liquids compounded with film-forming substances to produce bonded dry films, synthetic resins and powder metal compositions containing graphite for bearings, and finely divided suspensions in liquids (colloidal graphite).

High temperature lubrication, as in some metal-forming processes, requires dry graphite. Although the coefficient of friction of graphite is higher than that of petroleum lubricants, it is often added as a safety measure should the carrier lubricant fail (17) (see LUBRICATION AND LUBRICANTS).

Brake Linings. Substantial amounts of crystalline flake, lump, and amorphous graphite are used in brake and clutch linings, mostly in heavier duty nonautomotive situations. The graphite has been substituted for asbestos because of health considerations. The graphite proportion of the part has risen from 2 to 15% in some instances. The graphite lubricates, transfers the heat of friction away from the lining, and lowers the rate of wear.

Expanded Graphite. This is an important new use for crystalline flake graphite. Expanded graphite is made by treating crystalline flake graphite with chromic and sulfuric acid and then heating it until the water between the crystals (plates) of graphite is driven off to cause expansion. It is used as hot topping to keep the heat inside of an ingot, as a gasket material in applications subject to high temperatures and pressures, and in graphite foil.

Colloidal Graphite. Colloidal graphite refers to a permanent suspension of fine, natural, or synthetic graphite in a liquid medium. The average particle size is about 1 μm and protective colloids ensure permanency of the suspension. Film-forming binders may also be present. The name semicolloidal is applied to less stable dispersions, ie, those that settle more readily because of larger particle size, less effective processing, or both. In stable suspensions, the lower limit of size is controlled by the smallest size that can retain graphitic structure (Fig. 2).

Pencils. The lead pencil (18), so-called because of the black lead (natural graphite) on which its marking property depends, is essentially a baked ceramic rod of clay-bonded graphite encased in wood. Some plastic-bonded leads are now manufactured. The quality of the lead depends on the quality of the ingredients and the manufacturing process; the degree of hardness depends on the ratio of clay to graphite. The clays are selected and refined secondary clays; the graphites are of a variety of purities, particle sizes, and kinds. Amorphous graphites are usually used in the cheaper grades of leads. The best leads use a mixture of graphites dictated by carefully controlled testing.

A common procedure of lead manufacture is to ball-mill or hammer-mill a water slurry of the clay and graphite, dry the slurry, mix into a stiff dough

in an intensive mixer, compact into an extrusion cylinder, and extrude under pressure through a die. The wet strands are dried, packed in saggers, and kiln-fired at temperatures of 800–1100°C. The fired leads are then impregnated with waxes, fats or fatty acids, or both. The waxed leads are surface-cleaned and glued between grooved cedar slats, shaped into pencil sections, lacquered, and imprinted.

The degree of hardness is regulated principally by the clay-to-graphite ratio. Increasing the clay percentage strengthens the lead, thereby increasing its resistance to abrasion with a result that less graphite is deposited on the paper and the mark is less dense. In writing pencils, No. 1 lead contains ca 20% clay and No. 4 (hardest) has ca 60% clay.

Electrical Uses. Dry cells (see BATTERIES, PRIMARY CELLS) use graphite to render the nonconductive pyrolusite (MnO_2) conductive through intimate admixture. The degree of graphitization is a factor in that graphites with the same carbon content and from the same locality give different results.

Natural graphite is required in some motor and generator brushes. Its high conductivity, high contact drop, and anisotropy make it particularly useful in brushes for d-c equipment.

Paint. Some graphites act as reinforcing pigments which aid in the formation of tough, flexible, durable protective coatings (19). The platelike structure of graphite and its "leafing" produce films of low permeability. The paints are used for protecting structural steel and other metal surfaces exposed to unusually rigorous conditions or chemical attack, including water tank interiors. The gray color of graphite is its one drawback, limiting its use to dark-colored paints. Its unctuousness is important for automobile primers to upgrade the sanding properties as well as to improve brushing and flow properties for further coating applications. Graphite is admixed with other pigments, such as iron oxide, for primers. It may be used singly or combined in intermediate and top coats (see COATINGS).

Powder Metallurgy. Natural graphite is increasingly used in powder metallurgy as a solid lubricant constituent in bearing products and as a source of carbon in steel products. Graphite is added at the mixing operation in percentages ranging from 0.2 to 25% by weight. It serves to lubricate the die in the compacting operation and to reduce metallic oxides during the sintering operation to form steel, as well as serving as a lubricant during pressing.

Miscellaneous Uses. Minor uses of graphite include coating smokeless powder and gunpowder grains to control burning rate and prevent static sparking from friction between grains, roofing granules, packings, gaskets, stove polish, static eliminator, polish for tea leaves and coffee beans, pipe joint compounds, boiler compounds, wire drawing, welding rod coatings, catalysts , oil-well drilling muds, lock lubrication, coatings for 8-track tape cartridges, mechanical mounts in cassettes, mercury and silver dry cells, exfoliated flake for gaskets and packing, aircraft disk brakes, catalyst pellet production, O-rings and oil seal, and interior and exterior coatings for cathode ray tubes. In Europe colloidal graphite is added to lubricating oil for gasoline and diesel engines.

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